Hydrochemical properties and influencing factors of nitrogen pollution for shallow groundwater in the Urban planning area of Suzhou City

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Abstract. Detailed study of the chemical analysis results of 14 shallow groundwater samples, representing different land use types, were carried out in an attempt to identify the hydrochemical properties and influencing factors of nitrogen pollution for the Urban planning area in Suzhou city, China. Hydrochemical properties were analyzed by water quality and its’ main influential factors of nitrogen pollution were analyzed by using ArcGIS geostatistics module and factor analysis method. The results show that the water chemistry type of shallow groundwater in the study area was mainly HCO₃⁻-Ca-Na type, the shallow groundwater was in a strong reducing geological environment rich in organic matter. Shallow groundwater shows a significant nitrogen occurrence with high ammonia and low nitrate owing to the strong reducing geological environment with abundant organic matter and low oxygen in the study area. The occurrence forms of nitrogen in shallow groundwater were controlled by the oxidation-reduction environment. Factor analysis shows that the nitrogen content and pollution of shallow groundwater are mainly controlled by human activities and geological conditions, followed by formation lithology, redox conditions and topography.

1. Introduction
The shallow groundwater system not only has a direct connection with surface water bodies and aeration zone, but also has a close hydraulic connection with deep groundwater. As the buffer media of surface water and deep groundwater, shallow groundwater is highly susceptible to nitrogen pollutants and easily becomes a nitrogen storage reservoir under different meteorological and hydrogeological conditions [1]. At present, the nitrogen load level of environmental water bodies in the Yangtze River Delta remains high, and it has become the most common pollution factor for surface water and groundwater. Studies have found that there are various degrees of nitrogen pollution in shallow groundwater in many parts of the Taihu Lake Basin. In some area, Nitrate concentration and over-standard rate in the groundwater are both high [2] [3]. Nitrogen pollution prevention and control will be a long-term and arduous task of groundwater pollution prevention and control work [4] [5].

As a city with rapid economic development activities and dense population, the industrialization and urbanization process in urban planning area of Suzhou city are very fast. However, little is known about the major hydrochemical properties that control the observed chemistry of shallow groundwater and key influencing factors of nitrogen pollution in the region. The main purposes of this case study are: (1) to identify the hydrochemical properties and quality of shallow groundwater in the urban planning area...
of Suzhou city; (2) to identifies and determines the characteristics of nitrogen occurrence and nitrogen pollution influencing factors.

2. Materials and methods

2.1. Study Area
This study was located in the eastern part of the Taihu Lake Basin (Fig.1). The territory is dominated by gentle plain terrain; the terrain is low and flat, high in the northwest and low in the southeast. The ground elevation is generally 3.5-5 m (Wusong elevation); the rivers and lakes in the territory are densely covered with stagnant water bodies, which are typical plain river network areas. The area has a humid subtropical climate with four distinct seasons, a mild climate and abundant rainfall. The average annual temperature is 15-16℃, average annual precipitation is about 1000-1200 mm and annual land evaporation is 750-800 mm, and the annual water surface evaporation is about 1000 mm. The shallow groundwater system in the study area was mainly composed of phreatic water and micro-confined water aquifers shallower than 50 meters below the surface.

![Figure 1. Location of the study area and sampling sites](image)

2.2. Sample sites and sample collection
To evaluate and identify the shallow groundwater quality and hydrochemical properties, 14 long-term key monitoring points of shallow groundwater in different types of representative areas in Suzhou urban planning area were selected (Fig.1). NO.1-4 were located in the old urban area, NO.5-9 were in the new urban area, and NO.10-14 were located in the suburban and rural areas of the cities. Water samples were collected using a liquid sampler (SEBA, Germany); after being pumped for 10-15 minutes, all collected samples were stored in precleaned polyethylene bottles stored at 4 ℃ and then immediately transported to the laboratory for immediate analysis.

2.3. Sample analysis
Samples were measured for water depth (H), water temperature (T), pH, dissolved oxygen (DO), redox potential (Eh), electrical conductivity (EC) and total dissolved solids (TDS) in the field. Among them, H was measured by fixed depth sampler meter, T and DO were measured by SG6 type dissolved oxygen meter, pH and Eh were measured by PHPJ-260 type pH meter, TDS and EC were measured by DDBJ-350 type conductivity meter. The anions and cations were measured standard methods issued by National Environmental Protection Administration of China [6].
2.4. Data analysis
SPSS 19.0 software was used for statistical analysis, ArcGIS 10.5 was used to draw the spatial distribution map of sampling points and parameters, and origin 8.0 was used to draw the data map.

3. Results and discussion
3.1. Hydrochemical properties of shallow groundwater
The main physical and chemical indicators of shallow groundwater were listed in Table 1. It could be seen that the depth of shallow groundwater was 0.45-5.40 m, with an average of 2.51 m, and the groundwater table was shallow. The pH value was 6.09-9.54 (with an average of 7.29), which was generally neutral except for individual points. EC was 353-2520 μS/cm, and most samples were around 1000 μS/cm. Eh was -149-94 mV, with a large variation range, with an average value of -2.62 mV and a large coefficient of variation. TDS was 387-1565 mg/L, with an average of 792.44 mg/L. Among the main cations, the average contents of Na\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) were 61.86±24.18 mg/L, 88.63±24.46 mg/L and 23.92±7.66 mg/L, respectively, and the coefficients of variation were 0.39, 0.28 and 0.32, respectively, showing small spatial differences. Among the main anions, the average values of HCO\(_3\)\(^-\), Cl\(^-\) and SO\(_4\)\(^{2-}\) were 343.44±100.34 mg/L, 74.48±42.46 mg/L and 66.51±42.46 mg/L, respectively, and the coefficient of variation was small. According to the analysis of the concentration of main anions and cations, the order of the average cation content was Ca\(^{2+}\)> Na\(^+\)>Mg\(^{2+}\), the order of anion content was HCO\(_3\)\(^-\)> Cl\(^-\)>SO\(_4\)\(^{2-}\), HCO\(_3\)\(^-\) was the main anion form, and the main water chemical type of shallow groundwater in the study area was HCO\(_3\)-Ca-Na type.

| Indicator | Unit | Minimum | Maximum | Average | Variance | Coefficient of variation (CV) | Class III Standard Limits for GW \[^7\] |
|----------|------|---------|---------|---------|----------|-------------------------------|---------------------------------|
| H        | m    | 0.45    | 5.40    | 2.51    | 1.23     | 0.49                          |                                 |
| T        | °C   | 11.50   | 27.80   | 20.63   | 3.50     | 0.17                          |                                 |
| pH       |      | 6.09    | 9.54    | 7.29    | 0.78     | 0.11                          | 6.5-8.5                        |
| DO       | mg/L | 0.36    | 7.13    | 2.57    | 1.48     | 0.58                          |                                 |
| Eh       | mV   | -149.00 | 94.00   | -2.62   | 46.95    | 17.94                         |                                 |
| EC       | μS/cm| 353.00  | 2520.00 | 1077.61 | 398.74   | 0.37                          |                                 |
| TDS      | mg/L | 387.00  | 1565.00 | 792.44  | 276.34   | 0.35                          | 1000                           |
| DOC      | mg/L | 7.21    | 345.70  | 102.29  | 85.84    | 0.84                          |                                 |
| COD\(_{\text{BOD}}\) | mg/L | 0.96    | 17.49   | 5.81    | 3.83     | 0.66                          | 3.0                            |
| TN       | mg/L | 0.92    | 30.40   | 8.23    | 8.23     | 1.00                          |                                 |
| TP       | mg/L | 0.03    | 2.92    | 0.42    | 0.70     | 1.65                          |                                 |
| Na\(^+\) | mg/L | 35.00   | 119.00  | 61.86   | 24.18    | 0.39                          | 200                            |
| Ca\(^{2+}\) | mg/L | 54.60   | 144.00  | 88.63   | 24.46    | 0.28                          |                                 |
| Mg\(^{2+}\) | mg/L | 14.60   | 38.90   | 23.92   | 7.66     | 0.32                          |                                 |
| HCO\(_3\)\(^-\) | mg/L | 219.00  | 638.00  | 343.44  | 100.34   | 0.29                          |                                 |
| Cl\(^-\) | mg/L | 21.80   | 189.00  | 74.48   | 42.46    | 0.57                          | 250                            |
| SO\(_4\)\(^{2-}\) | mg/L | 11.00   | 148.00  | 66.51   | 43.87    | 0.66                          | 250                            |
| Fe       | mg/L | 0.02    | 2.60    | 0.54    | 0.71     | 1.33                          | 0.3                            |
| Mn       | mg/L | 0.01    | 1.46    | 0.44    | 0.48     | 1.07                          | 0.1                            |
| Total Hardness | mg/L | 199.00  | 520.00  | 319.75  | 88.30    | 0.28                          | 450                            |
| Total Alkalinity | mg/L | 180.00  | 523.00  | 288.88  | 81.71    | 0.28                          |                                 |

The content of iron and manganese in shallow groundwater was relatively high, the content of which were 0.54±0.71 mg/L and 0.44±0.48 mg/L, respectively, all exceeding the Class III limit of groundwater quality standard (GB/T14848-2017) \[^7\], the coefficients of variation were large (1.33 and 1.07 respectively), and the spatial differences were large. The DOC content was 7.21-345.70 mg/L, the
average was 102.29 mg/L, and the coefficient of variation was 0.84; the COD$_{Mn}$ content was 0.96-17.49 mg/L, the average was 5.81 mg/L, indicating that the groundwater pollution by organic and inorganic oxidizable substances degree was high, and the spatial difference was medium. The content of DO was 0.36-7.13 mg/L, the average is 2.57 mg/L, and the coefficient of variation is low (0.58). The Eh value of shallow groundwater was mostly negative, with an average value of -2.62 mV. The shallow groundwater exhibited high content of DOC, COD$_{Mn}$, HCO$_3$ and low content of DO, indicating that the study area was in a strongly reducing geological environment rich in organic matter.

3.2. Characteristics of nitrogen occurrence in shallow groundwater

In natural water bodies, nitrogen exists in many forms, and nitrogen of different valences can be transformed through reactions such as mineralization, ammonia oxidation, nitrification, denitrification, and alienation reduction[2]. According to the occurrence and distribution characteristics of different forms of inorganic nitrogen in aqueous solutions, and considering the distribution of natural phreatic water, the theoretical distribution relationship among various forms of inorganic nitrogen and pH and Eh in the groundwater environment can be drawn[8]. The measured data of pH and Eh were nested in the relationship diagram, and the bubble map of inorganic nitrogen and pH-Eh in the study area was drawn (Fig.2) to infer the occurrence form of nitrogen in shallow groundwater. From the analysis in Figure 10, it could be seen that most of the measured data at the sampling points fall in the NH$_4^+$ zone (only a few points fall in the NH$_3$ zone), and were obviously biased to the side of the water reduction area. This indicated that the shallow groundwater inorganic nitrogen was mainly NH$_4^+$-N instead of NH$_3$ as the main occurrence form, and also showed the chemical characteristics of reducing water.

The forms of nitrogen in groundwater are mainly affected by many factors, such as hydrogeological conditions, pH, redox potential, biological and human activities [2] [9]. The redox environment of groundwater has an important influence on the relationship between ammonia nitrogen and nitrate content in groundwater [10]. Table 1 showed that shallow groundwater had higher concentrations of Fe-Mn, DOC, COD$_{Mn}$ and lower Eh and DO. This indicated that the shallow aquifer in the study area was rich in organic matter and reducing substances, and the groundwater had a low redox potential, which also indicated that the shallow groundwater was in a relatively strong hypoxic and reducing environment. Relevant studies had shown that an environment with higher organic matter content and lower dissolved oxygen was more conducive to denitrification by denitrifying bacteria, so nitrate nitrogen was consumed in large quantities and the concentration was reduced [11]. High-concentration ammonia nitrogen may be produced by various methods such as organic nitrogen mineralization, nitrate dissimilative reduction (DNRA), and a large amount of ammonia-containing pollutants on the ground through the infiltration of the vadose zone [12]. It was generally believed that the increase of ammonia nitrogen concentration in the reaction layer or aquifer was mainly due to the occurrence of DNRA. The strength of DNRA was affected by the hypoxic environment and the content of organic matter [10] [12]. Figure 3 showed that
the relatively high content of ammonia nitrogen in the shallow groundwater in the study area corresponded to the low content of nitrate nitrogen, which was obviously different from the pollution characteristics of high content of nitrate nitrogen and low ammonia nitrogen in groundwater in other adjacent areas of the Yangtze River Delta [3]. This indicated the influence and control of the reducing geological environment on the occurrence of nitrogen, and there may be strong denitrification and nitrate dissimilation and reduction in the shallow groundwater in the study area. The characteristics of nitrogen occurrence in shallow groundwater in the study area were as followed: The redox environment affected and controlled the nitrogen occurrence form of shallow groundwater. Affected by the rich organic matter, low oxygen and strong reducing primary geological environment, inorganic nitrogen was the main body of nitrogen in shallow groundwater in the study area. Ammonia nitrogen was the main existing form of inorganic nitrogen, showing significant nitrogen occurrence characteristics with high ammonia nitrogen and low nitrate nitrogen.

3.3. Analysis on influencing factors of nitrogen pollution in shallow groundwater

3.3.1 Factor Analysis. Factor analysis transforms multiple chemical indicators of groundwater into potential hypothetical variables that can reflect its main information through dimensionality reduction analysis, that is, extracting and collecting groundwater hydrochemical indicators to effectively identify its pollution factors, which is one of the effective methods in identifying groundwater nitrogen pollution. In this study, H, pH, Eh, EC, TDS, CODMn, TN, Na⁺, Ca²⁺, Mg²⁺, HCO₃⁻, Cl⁻, SO₄²⁻, Fe, Mn, NH₄⁻-N, NO₃⁻-N and NO₂⁻-N were selected from the water quality analysis indicators, as the main indicators of factor analysis. First, standardized the index data, and then used SPSS19.0 software to perform factor analysis. Selected factors with Eigenvalues greater than 1 as common factors. Five common factors were selected. The eigenvalues, variances and cumulative variances are shown in Table 2.

| Ingredient | Decimated Sum of Squares Loading | Rotate the Sum of Squares Loading |
|------------|---------------------------------|---------------------------------|
|            | Eigenvalues | Variance (%) | Total (%) | Eigenvalues | Variance (%) | Total (%) |
| F1         | 5.852       | 32.509       | 32.509    | 5.270       | 29.275       | 29.275    |
| F2         | 3.693       | 20.519       | 53.028    | 2.822       | 15.678       | 44.953    |
| F3         | 2.577       | 14.319       | 67.347    | 2.759       | 15.330       | 60.283    |
| F4         | 1.887       | 10.485       | 77.832    | 2.352       | 13.067       | 73.349    |
| F5         | 1.116       | 6.201        | 84.033    | 1.923       | 10.684       | 84.033    |

It could be seen from Table 2 that the variance explained by the 5 common factors accounted for 84.033% of the total variance, and the cumulative contribution rate did not change before and after the
rotation, and there was no loss of information, which can more comprehensively reflect the basic information of the original variables. The factor F1 variance contribution rate after rotation was 29.275%, while the factor F2, F3, F4, F5 variance contribution rate were 15.678%, 15.330%, 13.067%, 10.684%, respectively, the four factors were not much different. The results showed that factor F1 may be the main influencing factor of nitrogen pollution in shallow groundwater, while factors F2, F3, F4 and F5 had more important contribution to nitrogen pollution.

3.3.2 Identification of influencing factors of nitrogen pollution. The factor load matrix was obtained by orthogonal variance maximum rotation method. The two ends of the rotated factor load matrix were concentrated, which can better explain the main factors.

**Table 3. Load factor matrix after orthogonal variance maximum rotation.**

| Indicator | F1    | F2    | F3    | F4    | F5    |
|----------|-------|-------|-------|-------|-------|
| H        | -0.360| -0.235| -0.247| 0.651 | 0.274 |
| pH       | -0.471| -0.019| -0.196| 0.769 | -0.110|
| Eh       | -0.164| -0.070| -0.193| -0.763| 0.355 |
| EC       | 0.685 | 0.516 | 0.226 | -0.045| -0.128|
| TDS      | -0.053| 0.007 | 0.730 | 0.015 | 0.062 |
| CODMn    | 0.852 | 0.000 | 0.279 | -0.072| -0.201|
| TN       | 0.935 | -0.204| 0.107 | -0.038| -0.044|
| Na+      | 0.297 | -0.112| 0.421 | 0.004 | -0.839|
| Ca2+     | -0.158| 0.738 | 0.170 | -0.045| 0.583 |
| Mg2+     | 0.053 | 0.296 | 0.510 | -0.296| 0.674 |
| HCO3−    | 0.050 | -0.226| 0.886 | -0.224| -0.143|
| Cl−      | 0.037 | 0.886 | 0.078 | -0.051| -0.039|
| SO4^{2-} | -0.174| 0.813 | -0.263| -0.031| 0.274 |
| Fe       | -0.261| -0.461| -0.753| 0.086 | 0.145 |
| Mn       | 0.385 | -0.065| -0.179| 0.768 | 0.049 |
| NH4^+    | 0.877 | 0.100 | -0.068| 0.041 | 0.040 |
| NO3^−    | 0.899 | -0.284| 0.038 | 0.003 | -0.096|
| NO2^−    | 0.936 | 0.075 | -0.139| 0.051 | -0.133|

It can be seen from Table 3 that F1 was the combination of EC, CODMn, TN, NH4^+ -N, NO3^− -N and NO2^− -N, all of which were positively loaded. CODMn reflected the geological environment rich in organic matter. EC reflected concentration of anions and cations in the water. If the groundwater was polluted to a certain extent, its EC value would increase significantly. Therefore, F1 can be regarded as the influence of geological conditions and man-made pollution factors on nitrogen content of shallow groundwater. F2 was mainly controlled by Ca^{2+}, Cl−, SO4^{2−} and other indicators, and they were all positively loaded. Ca^{2+} and SO4^{2−} were the main indicators to control the salt content of groundwater, and their size was significantly affected by the lithology of the formation. Cl− mainly came from the production of human activities and discharge of domestic sewage [13], and was significantly affected by human activities. Therefore, F2 can be regarded as an influencing factor of stratum lithology and human pollution. F3 was the combination of TDS, HCO3− and Fe. TDS and HCO3− were positive loads, representing salt content of the aquifer, which can be approximately regarded as the influence of geological conditions. The negative load of Fe indicated the effect of redox conditions on nitrogen content. Therefore, F3 can be regarded as the influence factor of geological conditions and redox conditions. F3 was the combination of H, pH, Mn, and Eh. H represented the depth of water level. The deeper the water level was, the aquifer changed from an oxidizing environment to a reducing environment. At the same time, both Mn and H were positive loads, showing the effect of redox
conditions on nitrogen content. The depth of groundwater was mainly affected by topography. Eh was a negative load, which also showed the influence of redox environment on nitrogen content. Therefore, F4 can be regarded as the influence factor of topography and redox conditions. F5 was a combination of Na⁺ and Mg²⁺, representing the level of dissolved salt in the shallow aquifer, which was mainly affected by natural water-rock interaction. Therefore, F5 can be regarded as an influence factor of geological conditions.

4. Conclusion

- The major hydrochemical type of shallow groundwater in the study area was HCO₃-Ca·Na type, and the range of Eh variation was relatively large, with an average value of -2.62mV. The contents of Fe, Mn, CODMn and DOC were all high, but the DO was low. The shallow groundwater was in a strong reducing geological environment rich in organic matter.
- The redox environment affected and controlled the nitrogen occurrence form of shallow groundwater, and was affected by the original geological environment rich in organic matter, low oxygen and strong reduction. Inorganic nitrogen was the main body of nitrogen in shallow groundwater in the study area, while ammonia nitrogen was the main form of inorganic nitrogen. It presented a significant characteristic with high ammonia nitrogen and low nitrate nitrogen occurrence.
- Factor analysis showed that main influencing factors of nitrogen pollution status, occurrence characteristics and distribution characteristics of shallow groundwater were man-made pollution factors and geological conditions, followed by stratum lithology, redox conditions and topography.

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