Characteristics of nitrogen pollution for shallow groundwater in typical urban planning area in Taihu Lake Basin

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Abstract. In order to verify the nitrogen pollution status of shallow groundwater in typical city of Taihu Lake Basin, urban planning area of Suzhou city was selected as the study area, and 14 sampling sites representing different land use types were selected to carry out water quality analysis. The status, temporal variability of nitrogen pollution and composition characteristics of various forms of nitrogen for shallow groundwater were analyzed. The results show that the nitrogen pollution of shallow groundwater in study area is relatively serious. The average contents of total nitrogen, dissolved inorganic nitrogen, total organic nitrogen, ammonia nitrogen, nitrite nitrogen and nitrate nitrogen are 8.23, 5.45, 2.77, 2.53, 0.12 and 2.81 mg/L, respectively. The variation coefficients of various forms of nitrogen are large and the spatial differentiation is significant. The contents of ammonia, nitrite and nitrate in shallow groundwater show an obvious spatial distribution characteristics. Nitrogen pollution in old urban areas is much more serious than other types of areas, especially ammonia nitrogen pollution is particularly prominent. Inorganic nitrogen is the main form of nitrogen in groundwater, while ammonia nitrogen is the main form of inorganic nitrogen.

1. Introduction
Nitrogen Contamination of the groundwater is one of the increasingly serious environmental problems in the world, and it is also a hot and difficult problem that domestic and foreign scholars are generally concerned about [1] [2] [3]. In recent years, due to large-scale agricultural production activities, large amounts of industrial wastewater and domestic sewage, and a significant increase in wet and dry deposition of atmospheric nitrogen compounds, the pollution of groundwater by excessive nitrogen content has become more and more prominent [4] [5] [6]. Human activities have caused changes in the nitrogen balance in terrestrial ecosystems, and significantly increased the nitrogen content in groundwater in many domestic and foreign areas, especially in shallow groundwater where the nitrogen severely exceeded the standard [7] [8].

Urban Planning Area of Suzhou City has dense population, rapid economic development, and frequent industrial and agricultural production activities. The water system in the territory is developed and frequently stagnant, which is a typical plain water network area in the Taihu Lake Basin. In recent years, the completely ban on extraction of deep groundwater and the heavy pollution of the surface water body bring people more and more attention to the abundant shallow groundwater resources [9]. Studies have shown that the shallow groundwater in the Suzhou area is buried shallow and thus easy to mine, but the water quality has been polluted to varying degrees [10] [11], which restricts the development,
utilization and effective protection of shallow groundwater resources to a certain extent [12]. The study takes Suzhou urban planning area as the research object. Through the long-term monitoring and analysis of shallow groundwater quality, the article studies the nitrogen content of shallow groundwater, and systematically analysis the spatial distribution of nitrogen. This case study is expected to provide basis and reference for the nitrogen pollution control and treatment of the shallow groundwater in this area and the Taihu Lake Basin.

2. Materials and methods

2.1. Study Area

This study was located in the eastern part of the Taihu Lake Basin (Fig.1). 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. The buried depth of the phreatic aquifer groundwater table is relatively shallow, the phreatic level is generally 0.5-4 m, and the lithology is mainly clayey soil, sandy loam and silt loam, with poor water richness. Phreatic water is obviously affected by climatic conditions. Atmospheric precipitation and surface water are its main sources of replenishment, and the main drainage methods are evaporation and artificial mining. The micro-confined aquifer is composed of a single layer or multiple layers of silt fine sand, with a thickness of 5-20 m and large spatial variations, and is closely related to the phreatic aquifer hydraulically. The micro-confined aquifer mainly receives the vertical cross-flow replenishment from the diving and the runoff is weak, and the main drainage channels are artificial mining and cross-flow recharge to the lower aquifer.

2.2. Sample sites and sample collection

Based on the preliminary research, 14 long-term key monitoring points of shallow groundwater in different types of representative areas in Suzhou urban planning area were selected (Fig.1). Among them, sampling points 1-4 were located in the old urban area, sampling points 5-9 were in the new urban area, and sampling points 10-14 were located in the suburban and rural areas of the cities. In terms of aquifer type, sampling points 4 and 8-10 were micro-confined water, and the rest were phreatic water. Submersible pump was used to pump water for 10-15 minutes before sampling, or the groundwater depth sampler (Germany SEBA) was used to collect samples. The samples were stored within 24 hours or at 4 °C and then taken back to the laboratory for immediate analysis.

2.3. Sample analysis

The field measurement indicators included water depth (H), water temperature (T), dissolved oxygen (DO), pH, redox potential (Eh), electrical conductivity (EC), total dissolved solids (TDS), etc.
nitrogen (TN), ammonia nitrogen (NH$_4^+$-N), nitrate nitrogen (NO$_3^-$-N) and nitrite nitrogen (NO$_2^-$-N) were measured standard methods issued by National Environmental Protection Administration of China [13]. Dissolved inorganic nitrogen (DIN) was the sum of the mass concentrations of NH$_4^+$-N, NO$_3^-$-N, and NO$_2^-$-N, and total organic nitrogen (TON) is the difference between TN and DIN.

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. Nitrogen pollution situation of shallow groundwater
Average value, variance, coefficient of variation and excess rate of different forms of nitrogen for shallow groundwater in the study area are shown in Table 1. The results show that the detection rates of different forms of nitrogen were all 100%, and the contents of TN, DIN and TON were 0.92-30.40 mg/L, 0.20-26.94 mg/L and 0.13-12.53 mg/L, respectively. The average values were 8.23 mg/L, 5.45 mg/L and 2.77 mg/L, respectively. The coefficients of variation were 1.00, 1.26 and 0.95, respectively.

Generally, the content of NH$_4^+$-N was 0.01-19.87 mg/L, the average value was 2.53 mg/L, and the over-standard rate was 72.00%. The maximum value and average value were 39.74 times and 5.06 times of Class III standard limit, respectively. The content of NO$_2^-$-N was 0.002-1.640 mg/L, with an average value of 0.120 mg/L. The exceeding standard rate was only 1.33%, and the maximum value was 1.64 times of the Class III standard limit. The content of NO$_3^-$-N was 0.01-16.03 mg/L, the average value was 2.81 mg/L, and the content was lower than the Class III standard limit (20 mg/L). The results showed that there were significant differences in the levels of NH$_4^+$-N, NO$_2^-$-N and NO$_3^-$-N in the study area. Compared with the groundwater quality evaluation method [14], the comprehensive classification of shallow groundwater quality in the study area was Class V, and the exceeding standard indicator of Class V was NH$_4^+$-N.

Table 1. Statistical analysis results of nitrogen content in shallow groundwater in the study area.

| Indicator | Detection rate (%) | Concentration (mg/L) | Coefficient of variation (CV) | Over Standard Rate | Maximum exceeding multiple | Class III standard limits for GW [14] |
|-----------|-------------------|----------------------|-------------------------------|--------------------|---------------------------|-------------------------------------|
| TN        | 100               | 0.92-30.40           | 8.23                          | 1.00               | -                         | -                                   |
| DIN       | 100               | 0.20-26.94          | 5.45                          | 1.26               | -                         | -                                   |
| TON       | 100               | 0.13-12.53          | 2.77                          | 0.95               | -                         | -                                   |
| NH$_4^+$-N| 100               | 0.01-19.87          | 2.53                          | 1.51               | 72.00%                    | 39.74                               |
| NO$_2^-$N | 100               | 0.002-1.64         | 0.120                         | 2.00               | 1.33%                     | 1.64                               |
| NO$_3^-$N | 100               | 0.01-16.03         | 2.81                          | 1.46               | 0                         | 20.00                              |

Coefficient of variation was an important characteristic parameter that reflected the deviation of the sample, which could reflect the degree of data dispersion and the spatial distribution difference of nitrogen. It could be seen from Table 1 that the coefficients of variation of NH$_4^+$-N, NO$_3^-$-N, and NO$_2^-$-N were 1.51, 2.00, and 1.46, respectively, and the coefficients of variation were all relatively large, indicating strong variability. The results showed that there are significant differences in the distribution within the study area. The above analysis showed that the nitrogen pollution in shallow groundwater in
the study area was relatively serious, and special attention should be paid to timely investigation and identification of pollution sources, and effective control of pollution channels.

The frequency distribution of nitrogen content was shown in Figure 2, and the content distribution and frequency of different forms of inorganic nitrogen were quite different. The frequency of NH$_4^+$-N was approximately normal distribution, and the main content ranges were concentrated in the three intervals of 0.5-1.5 mg/L, 2.0-5.0 mg/L, and 0.1-0.5 mg/L, with the frequency of 36.00%, 18.67% and 17.33%, respectively. The frequency of NO$_2^-$-N was similar to the cascade distribution, and the main content ranges were concentrated in the four intervals of <0.01 mg/L, 0.01-0.1 mg/L, 0.1-0.2 mg/L and 0.2-0.5 mg/L, with the frequency of 33.33%, 33.33%, 16.00% and 13.33%, respectively. The frequency of NO$_3^-$-N was also similar to the cascade distribution, and the main content ranges were concentrated in the four intervals of <1 mg/L, 1-3 mg/L, 3-5 mg/L and 5-8 mg/L, with the frequency of 52.00 %, 16.00%, 12.00% and 10.67%, respectively. Taking reference of NO$_3^-$-N $\leq$ 3.0 mg/L as the reference of non-polluted standard, percentage of shallow groundwater below standard reference level was 68%, while frequency of below Class III Groundwater Quality Standard value (20 mg/L) was 100%, indicating that most areas of the study area were not affected by NO$_3^-$-N pollution.

![Figure 2. The frequency distribution diagram of the content of nitrogen in shallow groundwater](image)

3.2. Spatial distribution characteristics of nitrogen pollution

The difference of spatial distribution of nitrogen content among different sampling points may be related to the difference of land use type in plane and aquifer depth in vertical direction. Land use type was often the main factor contributing to shallow groundwater pollution[15]. The statistical results of the “three nitrogen” content of shallow groundwater at sampling points in different land-use areas (old urban areas, new urban areas, suburban, and rural areas) were shown in Figure 4 and Table 5. It could be seen from Figure 3 that the average content of NH$_4^+$-N in the old urban area was the highest (5.56 mg/L), followed by the suburban, rural areas and new urban areas, with an average content of 0.85 and 0.61 mg/L, respectively. This indicated that the problem of groundwater NH$_4^+$-N pollution in the old urban area was particularly serious. The average content of NO$_2^-$-N in the old urban area was the highest (0.29 mg/L), followed by the suburban, rural and new urban areas, with the average content of 0.028 and 0.012 mg/L, respectively. The average content of NO$_3^-$-N in the old urban area was also the highest (5.71 mg/L), followed by the new urban area, suburban and rural areas, with the average content of 1.28 and 0.85 mg/L, respectively. In general, the order of nitrogen content in different land use types was: Old urban > new urban > suburban and rural areas. It could be seen from Table 2 that for different nitrogen indicators, the coefficient of variation between the three different land types under the same nitrogen indicator was not much different, and the coefficient of variation between different nitrogen indicators under the same land type was not much different, 1 or so.

In terms of plane distribution, the ArcGIS geostatistical module was used to analyze the spatial distribution characteristics of various forms of nitrogen in shallow groundwater in different regions (Fig. 4). It could be seen from the analysis in Figure 5 that the population density of the old urban area was high, and is the area with the worst underlying surface conditions. A large amount of domestic sewage, wastewater and rainwater was discharged into the river and the imperfect old drainage pipe network. Affected by many factors such as surface water seepage recharge shallow groundwater and drainage pipe network leakage, a large amount of nitrogen-containing pollutants would continue to accumulate.
into the shallow groundwater along with the river overflow recharge and pipe leakage, causing the shallow groundwater pollution in the old urban areas to be significantly higher than other land types. Therefore, the old urban area was the most serious area of shallow groundwater nitrogen pollution in the study area, and the nitrogen pollution was distributed by points or strips. Due to the perfect collection and treatment facilities of wastewater in the new urban area, the input of nitrogen pollutants into shallow groundwater was significantly less than that in the old urban area, thus the pollution degree was relatively light. The underlying surface conditions in the suburban and rural areas are better. Although there was a certain degree of agricultural non-point source pollution, atmospheric precipitation, surface water and shallow groundwater recharge and discharge were closely related, and the overall pollution degree was very light, showing the characteristics of surface distribution.

3.3. Composition characteristics of various forms of nitrogen

It could be seen from Figure 5 and Figure 6 that the characteristics of various forms of nitrogen in the shallow groundwater of each sampling point were relatively consistent. Except for a few points, most of the sampling points DIN:TON>1 (average 3.11), and the content of DIN and TON accounted for 66.22% and 33.78% of TN, respectively. This indicated that the content of inorganic nitrogen in most sampling points was significantly higher than that of organic nitrogen, and inorganic nitrogen was the main part of nitrogen in groundwater.
Generally speaking, the proportion of organic nitrogen in natural groundwater is very low, while in this study, organic nitrogen accounted for about 30% of total nitrogen, which indicated that the shallow groundwater in the study area may be affected by external input and significant man-made pollution. In the composition of inorganic nitrogen, from the absolute value of mass concentration and the proportion of composition, the average content of NO₃⁻N in most sampling points was the highest, accounting for 53.14% of DIN, which was not over standard. The average content of NH₄⁺-N was the second, accounting for 45.10% of DIN, but the over standard rate was high. The average content of NO₂⁻N was the lowest, accounting for only 1.76% of DIN, and the over-standard rate was also very low. From the above analysis, it could be seen that NO₃⁻N and NH₄⁺-N were the main forms of dissolved inorganic nitrogen DIN in the shallow groundwater of the study area.

Figure 5. DIN: TON ratio statistics of shallow groundwater at different sampling points

Figure 6. The percentages of different forms of nitrogen in various sampling points

4. Conclusion
- The average contents of TN, DIN and TON in shallow groundwater were 8.23, 5.45 and 2.77 mg/L, respectively. The average content of NH₄⁺-N, NO₂⁻-N and NO₃⁻-N in DIN were 2.53, 0.12 and 2.81 mg/L, respectively. The comprehensive category of shallow groundwater quality in the study area was Class V, and the Class V over-standard index was NH₄⁺-N. Compared with other regions in China, the shallow groundwater nitrogen pollution problem in the study area was more serious, especially the ammonia nitrogen pollution problem should be paid special attention.
- The spatial distribution characteristics of the nitrogen indicated that the spatial variability for different land-use types was large, and the NH₄⁺-N pollution problem in the old urban areas was particularly serious, and it was greatly affected by human activities.
- The composition characteristics of various forms of nitrogen showed that inorganic nitrogen
was the main part of nitrogen in groundwater. NO$_3^-$-N and NH$_4^+$-N were the main forms of dissolved inorganic nitrogen.

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