Migration and transformation of three nitrogen in groundwater and antipollution effect of aquitard in North China Plain typical area

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Abstract: The "three nitrogen" (NH$_4^+$-N, NO$_2^-$-N, NO$_3^-$-N) pollution of groundwater in north China plain region endanger the groundwater ecological environment. In this study, we chose the typical area of North China Plain as the representative research area. By numerical method, we analyzed the migration characteristics of "three nitrogen" pollutants in the 200 year time scale in different representative strata structural modes of shallow groundwater system in this area. Based on the simulation results, the retardant ability of the unit thickness of aquitard was analyzed. The results were as follows: (1) The migration of different kinds of "three nitrogen" pollutants in the aquifer system were different; (2) The strata structural characteristics have obvious effects on the migration of "three nitrogen", and their influence rules were different. The three representative strata structure models were constructed on the basis of comprehensive analyzing the regional strata features. Therefore, the simulation results have reference value for evaluation of the "three nitrogen" migration and the retardant ability of the aquitard in this area.

1. Introduction
Nitrogen pollution in groundwater is one of the most common and polluted groundwater pollution. Compounds of nitrogen, especially NH$_4^+$-N, NO$_2^-$-N and NO$_3^-$-N in ionic state, that is often known as "three nitrogen", have caused more and more attentions. The NH$_4^+$-N and NO$_3^-$-N are the mainly pollutions of "three nitrogen". For preventing nitrogen pollution in groundwater, that is of great significance to clarify the sources, influencing factors and migration rules of "three nitrogen" pollutants.

The sources of "three nitrogen" pollutants in underground water mainly include polluted surface water, pesticide and fertilizer, landfill leachate, waste water produced by industrial activities, etc. Agricultural irrigation and industrial sewage discharge are the main sources of nitrogen pollution in soil and groundwater.

The complexity of groundwater nitrogen pollution is mainly due to the complexity of nitrogen migration and transformation process. Studies have shown that under different land use conditions, the migration rule of "three nitrogen" pollutants was different. Even under the same land use conditions, the migration of the "three nitrogen" contaminants in the soil was also related to the rainfall, the physical and chemical properties of the crops and the layers, microstructure of the soil.

The existing researches were mainly about "three nitrogen" in the unsaturated zone of groundwater...
and surface water. The migration rule of "three nitrogen" pollutants in the saturated zone of groundwater aquifer needs to be further studied. In this paper, taken "three nitrogen" as the research object, a numerical model was constructed to analyze the migration characteristics of "three nitrogen" in typical representative saturated zone of shallow groundwater in in north China plain area. It is of great significance to prevent and control nitrogen pollution of shallow groundwater in typical area of North China Plain.

2. The characters of study area
The study area is located in the pollutants in north China plain area. The surface of the study area is mainly covered by Quaternary system, and the Quaternary sediments are widely distributed and more thinner. The thickness of the Quaternary sediments is controlled by paleo terrain. The lithology of the study area composes of grey, grey black, yellow clay, clayey silt, sandy silt, fine sand, medium coarse sand, gravel, and so on.

The single layer is generally not thick, and the strata structure are consist of interbededs of soil layer and sandy soil layer.

3. Simulation model and schemes

3.1 Establishment of the conceptual model
This simulation mainly studies the migration and transformation of "three nitrogen" in different groundwater aquifers in typical area of North China Plain from the angles of the aquifer structure, groundwater flow condition and the pollution degree of "three nitrogen". Three representative sites were selected (Figure 1). They are A type (the severe pollution area and the strata structure is the silty sand sandwiched clay structure, site A in Figure 1), B type (the severe pollution area and the strata structure is the medium-fine sand sandwiched clay structure, site B in Figure 1), C type (the slight pollution area and the strata structure is interbed structure of the silty sand, medium sand, clay, site C in Figure 1) The strata structures of the simulation sites see figure 2 to figure 4.

According to the geological and hydrogeological conditions of the A type area, the clay layer was set as a aquitard. The hydraulic conductivity of the silty sand was set as 2m/d, and its porosity was 35%; the hydraulic conductivity of clay was set as 0.001m/d and its porosity was 40%. Based on the site hydrogeologic condition, the strata structure and thickness and the groundwater level were depicted as a model shown in figure2.
According to the geological and hydrogeological conditions of the B type area, the clay layer was set as an aquitard. The hydraulic conductivity of the medium sand was set as 4.18 m/d and its porosity was 31.9%; the hydraulic conductivity of clay was set as 0.001 m/d and its porosity was 40%. Based on the site hydrogeologic condition, the strata structure, the thickness and the groundwater level were depicted as a model shown in figure 3.

According to the geological and hydrogeological conditions of the C type area, the clay layer was set as an aquitard. The hydraulic conductivity of the silty sand was set as 2 m/d and its porosity was 35%; the hydraulic conductivity of the medium sand was set as 17.32 m/d and its porosity was 35%; the hydraulic conductivity of clay was set as 0.001 m/d and its porosity was 40%. Based on the site hydrogeologic condition, the strata structure and the thickness and the groundwater level were depicted as a model shown in figure 4. The vertical one dimensional numerical model can be obtained by dividing the target layer model of A type, B type and C type. The vertical direction of each model was divided into 30 grids and the boundary conditions was shown in figure 2-figure 4, respectively.
3.2 Simulation scheme design

When we design simulation schemes, the key parameters and environmental condition must be ascertained first. The adsorption coefficient to the "three nitrogen" of different kinds of soil were assigned according to the adsorption test and the empirical values.

In this study, the chemical composition of the injected water was set according to the chemical composition of the local water. The concentration of "three nitrogen" pollutants in the groundwater was listed in Table 1.

| Code | Location | NO$_3^-$ (mol/L) | NH$_4^+$ (mol/L) | NO$_2^-$ (mol/L) |
|------|----------|------------------|------------------|------------------|
| 1    | A type   | < 10$^{-9}$      | 1.69 × 10$^{-5}$ | 7.07 × 10$^{-8}$ |
| 2    | B type   | 1.77 × 10$^{-4}$ | 9.64 × 10$^{-6}$ | 1.25 × 10$^{-6}$ |
| 3    | C type   | < 10$^{-9}$      | 7.91 × 10$^{-6}$ | 1.17 × 10$^{-6}$ |

By referring to the empirical value of transport velocity of "three nitrogen" pollutants in similar aquifer, the simulation time were set as 1 years, 10 years, 15 years, 20 years, 30 years, 50 years, 100 years, and 200 years. According to field investigation, the difference of water level between the phreatic aquifer and the first confined water level is 9 m~13 m. Thus the injection pressure was set to 1.078 × 10$^5$Pa (medium hydrodynamic condition, the difference of hydraulic head was 11m).

In this study, it is very difficult to determine the continuous time of pollution and the recharge strength of pollutants. Therefore, according to the data of the concentration of "three nitrogen" pollutants in Table 1, the "three nitrogen" pollutants were set continuously injected into the aquifer. The detailed simulation schemes was shown in Table 2.

| Scheme Code | strata structure | Hydrochemical characteristics | Injection pressure (pa) |
|-------------|------------------|------------------------------|-------------------------|
| 1           | clay in the middle of silty sand (A type area) | Chemical characteristics of injected water was same as the phreatic water samples | 1.078 × 10$^5$ |
| 2           | medium - medium fine sand sandwiched clay (B type area) | | 1.078 × 10$^5$ |
| 3           | interbed structure of clay, silty sand, clay and medium sand (C type area) | | 1.078 × 10$^5$ |
4. Results and discussion

When the hydrodynamic condition keeps constant, we can analyze the influence of different aquifer structures on migration and transformation of "three nitrogen" pollutants. Here we take the scheme 2 and scheme 3 as examples to analyze the effect of different strata structures on the migration and transformation of "three nitrogen" pollutants.

4.1 The migration of "three nitrogen" in scheme 2

The scheme 2 is one scenario of the B type area. The strata structure of scheme 2 is medium fine sand - medium sand sandwiched clay. The simulation results of scheme 2 were shown as figure 5–figure 7. According to figure 5 to figure 7, it can be seen that the transport time of the pollutant of NH$_4^+$-N, NO$_3^-$-N, NO$_2^-$-N from the surface of the unconfined aquifer to its bottom were around 10 years. NH$_4^+$-N, NO$_3^-$-N entered the confined aquifer from the top of the unconfined aquifer after around 16.4 years, 19.1 years, 19.1 years respectively.

Figure 5 The concentration of NH$_4^+$-N in the aquifer system varies with time

Figure 6 The concentration of NO$_3^-$-N in the aquifer system varies with time

Figure 7 The concentration of NO$_2^-$-N in the aquifer system varies with time

According to the time when NH$_4^+$-N, NO$_3^-$-N, NO$_2^-$-N migrated to the bottom of the unconfined aquifer and the top of confined aquifer. The lag time of NH$_4^+$-N, NO$_3^-$-N, NO$_2^-$-N from the bottom of the phreatic aquifer to the top of the first confined aquifer were 6.9 years, 9.1 years, and 8.2 years, respectively. The thickness of aquitard (clay) between the two aquifer is around 5 m. Therefore, the retardant ability of aquitard (clay) for NH$_4^+$-N, NO$_3^-$-N, NO$_2^-$-N were 0.72 m/a, 0.55 m/a and 0.61 m/a, respectively.

4.2 The migration of "three nitrogen" in scheme 3

The scheme 3 was one scenario of the C type area. The strata structure of scheme 3 is Silty sand - medium sand - clay interbed structure. The simulation results of scheme 3 were shown as figure 8–figure 10.

According to figure 8 to figure 10 and numerical simulation result data, it can be seen that the
pollutant of NH$_4^+$-N, NO$_3^-$-N, NO$_2^-$-N reached the bottom of the unconfined aquifer from the surface of the unconfined aquifer after around 2.7, 3, 3 years respectively. It started to enter the confined aquifer after around 19.1, 21.9, 22 years respectively.

![Figure 8 The concentration of NH$_4$+-N in the aquifer system varies with time](image)

![Figure 9 The concentration of NO$_3$--N in the aquifer system varies with time](image)

![Figure 10 The concentration of NO$_2$--N in the aquifer system varies with time](image)

According to the time when NH$_4^+$-N, NO$_3^-$-N, NO$_2$--N migrated to the bottom of the unconfined aquifer and the top of confined aquifer. The lag time of NH$_4^+$-N, NO$_3$--N, NO$_2$--N from the bottom of the phreatic aquifer to the top of the confined aquifer were 16.4 years, 18.9 years, and 18.9 years, respectively. The total thickness of aquitards (clay) is around 15 m. Therefore, the retardant ability of aquitards) for NH$_4^+$-N, NO$_3$--N, NO$_2$--N were 0.91 m/a, 0.79 m/a and 0.79 m/a, respectively. The effect of "three nitrogen" migration in other different aquifer structures were not discussed in detail here. And the data and results were shown in Table 3.

### Table 3 The retardant ability of the aquitard to "three nitrogen" pollutants migration

| Scheme Code | Location Description | Aquifer system structure and strum thickness (m) | NH$_4^+$-N | NH$_3^-$-N | NO$_3^-$-N | NO$_3$--N | NO$_2$--N | NO$_2$--N | Retardant ability of unit thickness of aquitard to "three nitrogen" (m/a.m) |
|-------------|----------------------|-----------------------------------------------|------------|-------------|------------|-----------|-----------|-----------|--------------------------------------------------|
| 1 A type area | Silty sand (14) - clay (7) - silty sand (9) | 8.0 | 8.0 | 6.8 | 17.8 | 17.8 | 13.6 | 0.71 | 0.71 | 1.03 |
| 2 B type area | Medium fine sand (17) – clay (5) - medium sand (8) | 9.5 | 10.0 | 10.9 | 16.4 | 19.1 | 19.1 | 0.72 | 0.55 | 0.61 |
| 3 C type area | Clay (4) - silty sand (5) – clay (6) - medium sand (4) – clay (5) - medium sand (6) | 2.7 | 3.0 | 3.0 | 19.1 | 21.9 | 21.9 | 0.91 | 0.79 | 0.79 |
4.3 The uncertainty of the simulation results

The three strata structure model in this study were based on a lot of geological boreholes in the study area. Due to the actual stratigraphic sedimentary structure in study area were very complicated, in the process of construct representative strata structure modes, some thin stratum were combined. When the aquifer system was mainly composed by sand layer to the thin discontinuous aquitard, it was merged into the sand layer and treated as the single sand layer. When the aquitard was continuous distribution and its thickness comparable to the sand layer thickness, it was generalized as interlayer structure.

For the areas generalized as single-layered structure in the northern and eastern part of study area, the discontinuous aquitard in the sand layer was not considered in the generalization of the model. Due to the discontinuous aquitard that was neglected in the actual strata formations has a blocking effect on the "three nitrogen" migration, therefore, the simulation results in this study have a certain extent of amplification effect in these areas, that is, the simulated migration time was shorter and the migration speed was faster than the actual circumstances.

In the area of the southern and Western of study area, the unconfined aquifers are mainly composed of fine sand, silty sand, and its surface is often covered with clay, and the aquitards mostly consist of clay and silt clay, and the first confined aquifers are composed of fine sand. In simulation, many simplification had been done to the conceptual model. The actual characters of the stratigraphic structure determines its retardant ability would be better than the simulation result.

5. Conclusion

Based on the hydrogeological condition of the study area, three typical representative strata structure modes were constructed. And then, combining the environmental characters of the study areas, numerical models were constructed to analyze the effects of different aquifer system structures and hydrodynamic characteristics on the migration of "three nitrogen" pollutants. The conclusions are as following:

1) The migration characters of different kinds of "three nitrogen" pollutants in the aquifer system were different. Taking the single layer structure in A type area as an example, the migration rate of nitrite nitrogen was the fastest.

2) The strata structural characteristics have obvious effects on the migration of "three nitrogen", and their influence rules were different. For the strata structure mode of silty sand sandwiched clay structure in A type area, under the same hydrodynamic condition, nitrite nitrogen had the fastest migration speed; and for the strata structure mode of medium - medium fine sand sandwiched clay structure in B type area, the ammonium nitrogen migration speed was the fastest; and for the strata structure mode of silty sand, medium sand and clay interlayer structure in C type area, also the ammonium nitrogen migration rate was the fastest.

3) The three representative models were broadly representative stratigraphic systems based on the comprehensive analysis of the characteristics of regional stratigraphy. Therefore, the simulation results have reference value for evaluation of the "three nitrogen" migration and the retardant ability of the aquitard in the study area.

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