Numerical simulation and prediction of chlorinated hydrocarbon migration in eastern Jinan

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Abstract. In this paper, the pollution of carbon tetrachloride in the Groundwater system is taken as the main research object. By selecting the monitoring sample points of shallow groundwater and using MT3DMS module in GMS numerical simulation software to establish the migration and transformation model of typical chlorinated hydrocarbons. Sequentially, predicting the development trend of carbon tetrachloride pollution. The results show that with the passage of time, the concentration of pollutants decreases due to the adsorption and attenuation of solid phase media, the pollution range of carbon tetrachloride decreases, and the overall pollution degree of carbon tetrachloride in karst water decreases. From the simulation results, the concentration time-duration curves of the typical points in different parts of the southern, central and northern parts of the pollution plume were extracted, and the linear equation was used for fitting. The fitting effect is good and conforms to the first-order attenuation equation, providing ideas for the prevention and treatment of chlorinated hydrocarbon pollution in the subsequent groundwater.

1. Introduction
As volatile organic compounds with a high detection rate in groundwater, chlorinated hydrocarbons are widely used in aircraft engines, automobile parts, electronic components and degreasing of clothes[1,2]. Such chlorinated solvents are non-aqueous (NAPLs), which are generally denser than water, less water-soluble, and not easy to degrade and remove, and most of them have carcinogenic effects or potential teratogenic (carcinogenic, teratogenic, mutagenic) hazards[3,4]. Common chlorinated hydrocarbon solvents include carbon tetrachloride, tetrachloroethylene, chloroform, trichloroethylene and trichloroethane. Chlorinated hydrocarbon pollutants enter the underground aquifer through a wide range of channels, the most important of which is the discharge of organic waste liquid and the leaching of precipitation. Besides, the volatilization of chlorinated hydrocarbons, the leakage during production and transportation, and the release of pesticides and fertilizers are also important sources of chlorinated hydrocarbons in the underground aquifer system[5]. Due to improper storage and disposal, chlorinated hydrocarbons enter the groundwater environment through leakage, wastewater discharge and other means, and have become a common organic pollutant in groundwater[6,7]. By simulating the migration of typical chlorinated hydrocarbons in the study area, the development trend of chlorinated hydrocarbons was predicted, which laid a theoretical foundation for further monitoring of organic pollutants in groundwater and exploring the control methods of organic pollutants in groundwater.
2. Overview of the study area
The study area straddled Jinan spring domain and Baiquan spring domain, with the Dongwu fault as the boundary. The water resistance property of the southern segment of the fault was obvious, and the part in the north showed weak water permeability. The two spring domains had a direct replenishment and drainage relationship in the area, but the area with weak water permeability was relatively small, and it was still a water resistance fault on the whole. There is a strong seepage zone in the south section of Daxin river in the southwest of the study area. This section is mainly quaternary ovoid and gravel layer with shallow burial depth and good permeability. The underlying layer is Cambrian Ordovician dolomitic limestone and dolomite. The Baiquan spring group in the northeastern part of the study area is the discharge area of Baiquan spring region, and the northern part is the carboniferous Permian formation, where the karst water runoff is blocked and exposed in a planar form.

3. Materials and methods

3.1. The conceptual model of Solute transport
Carbon tetrachloride was used as the research object to simulate the migration and transformation of chlorinated hydrocarbons in the groundwater system.

It is assumed that the kinetics of the dechlorination reaction can be approximated as a first-order reaction. Some studies have shown that the first-order kinetic reaction can be used to simulate the dechlorination mechanism of field polluted sites at low concentrations. The ordinary differential equations (ODEs) of the mechanical reaction of dechlorination of carbon tetrachloride are as follows:

$$\frac{dC_{CT}}{dt} = (\cdot k_{an} \cdot C_{CT} - k_{ab} \cdot C_{CT})$$  \hspace{1cm} (1)

$$\frac{dC_{CF}}{dt} = \left( Y_{CF} \cdot k_{an} \cdot C_{CT} - k_{an} \cdot C_{CF} \right)$$  \hspace{1cm} (2)

$$\frac{dC_{DCM}}{dt} = \left( Y_{DCM} \cdot k_{an} \cdot C_{CF} - k_{an} \cdot C_{DCM} - k_{ae} \cdot C_{DCM} \right)$$  \hspace{1cm} (3)

$$\frac{dC_{CM}}{dt} = \left( Y_{CM} \cdot F \cdot C_{DCM} \cdot C_{CM} - k_{an} \cdot C_{CM} - k_{ab} \cdot C_{CM} - k_{ae} \cdot C_{CM} \right)$$  \hspace{1cm} (4)

The dechlorination reaction module describes the dechlorination of carbon tetrachloride and related subproducts using a first-order rate expression. Some reaction pathways may not exist in this module, so it can be selectively closed by setting the constant value (spatially variable) of the chemometrics yield/reaction rate to zero in the simulation according to the actual situation.

3.2. Boundary conditions and initial conditions setting
Based on the distribution characteristics of pollution sources and the monitoring data of chlorinated hydrocarbon concentration in the groundwater system, the boundary conditions and initial concentration fields of the solute transport model were determined based on the boundary conditions of the flow model and the source and sink terms.

Lateral boundary: based on the spatial distribution characteristics and pollution range of carbon tetrachloride, the south and north boundary are generalized into the constant concentration boundary, and the value of 0.001μg/L is assigned to guarantee the migration of carbon tetrachloride within the study area. The east and west boundaries are generalized to zero flux boundaries.

The results of water sample analysis and tests show that the carbon tetrachloride pollution degree in the karst water system is the highest, showing the characteristics of surface pollution, especially in the east of the fault. The carbon tetrachloride pollution plume is distributed in an elliptic shape, and the water flow spreading from south to north everywhere has obvious pollution characteristics.
3.3. Migrate and transform model parameters
The main parameters considered in the solute transport model are porosity, dispersion coefficient, adsorption parameters, and degradation parameters. The porosity is mainly related to lithology. In this study, according to the collected historical research data, the porosity is 0.35, and the dispersion coefficient is the strength of the dispersion phenomenon that occurs when the solute penetrates through the soluble rock, which is related to the structure of the rock medium, the uniformity of the solute permeation path and the permeation velocity. According to the uniformity of the solute permeation path, the dispersion coefficient is divided into transverse dispersion coefficient, longitudinal dispersion coefficient, and vertical dispersion coefficient. In this study, the dispersion coefficient was calculated based on the data of previous dispersion tests in this region. The distribution coefficient was obtained from the isothermal adsorption of carbon tetrachloride by solid media. The degradation rate is substituted according to the calculated value of the biodegradation rate of chlorinated hydrocarbons in the previous section. In previous studies, two dispersion tests were conducted in the study area. One group was located in the northeast of Yihezhuang. The target aquifer of the dispersion test was the limestone of Majiagou formation. Another group of dispersion tests is located in the southwest of the study area. The target aquifer of the dispersion test is also the limestone of Majiagou formation. The data of two groups of dispersion tests were collected and the dispersion was calculated.

The parameters obtained from the dispersion test data are shown in table 1.

| Project                  | Longitudinal dispersion | Transverse dispersion | Molecular diffusion coefficient |
|--------------------------|-------------------------|-----------------------|--------------------------------|
| The dispersion group 1   | 1.6                     | 0.28                  | 1.81×10⁻⁷m²/d                  |
| The dispersion group 2   | 1.46                    | 0.25                  | 1.76×10⁻⁷m²/d                  |

Other parameters involved in the solute transport model are shown in table 2.
Table 2. The parameters of solute transport model

| Parameters                          | Values   |
|------------------------------------|----------|
| Severe (g/cm³)                     | ρ 1.5    |
| porosity                           | n 0.35   |
| The distribution coefficient (cm³/g)| Kd 61    |
| Degradation rate (l/d)             | 1.54×10⁻⁴|

4. Results and discussion

4.1. Simulations to predict

Aiming at the pollution status of chlorinated hydrocarbons in the karst water system, this study comprehensively studied the various effects of chlorinated hydrocarbons in the groundwater system and considered the adsorption and attenuation process of chlorinated hydrocarbons in the groundwater system. Comprehensive above chlorinated hydrocarbon isothermal adsorption experiment data, chlorinated hydrocarbon biodegradation water chemical characteristics of response and the biodegradation rate calculation, etc., with carbon tetrachloride as the research object, the absorption in the solute transport model coupling reaction and the attenuation, the MT3DMS module, open The Chemical Reaction Package package, input model-related parameters, to forecast the development trend of carbon tetrachloride pollution plume.

The development trend of carbon tetrachloride pollution plume in 2025, 2030, and 2040 is predicted respectively. The simulation results are shown in figure 2~4.

Figure 2. Contaminant plume in 2025

Figure 3. Contaminant plume in 2030
4.2. Results and discussion

(1) As can be seen from the figure, the plume of carbon tetrachloride pollution moved northward over time. Taking the W09 monitoring site in the north of the pollution plume as an example, under the initial conditions, the site was located at the edge of the pollution plume (figure 1). The model was migrated to 2030 and 2040, and W09 was gradually located at the center of the pollution in the north of the pollution plume, but the pollution level was less than before.

(2) From the developing trend of carbon tetrachloride pollution plume, and the pollution plume near the central belt of W01 and W14, carbon tetrachloride sharply reduce pollution degree, this is because the contaminant plume in the central zone, in a state of relative reduction of groundwater, and kinds of spatial distribution characteristic of water chemical composition also reflect the pollution plume in central zone state of groundwater environment conducive to carbon tetrachloride to biodegradation.

(3) At the same time, carbon tetrachloride pollution in W01, W14, and W06 zones along the plume axis was also reduced to varying degrees, reflecting that the concentration of carbon tetrachloride in groundwater system was reduced due to the adsorption and attenuation of solid-phase media during the migration and transformation of carbon tetrachloride.

(4) On the whole, with the passage of time, the pollution range of carbon tetrachloride pollution plume on the east side of the fault in the study area was reduced but not obvious, and the degree of carbon tetrachloride pollution in karst water was reduced.

5. Conclusions

By the pollution trend prediction graph can be seen that different parts of plume concentration of carbon tetrachloride were gradually decreasing trend, the three typical well point carbon tetrachloride concentration change over time trends for linear fitting, the fitting effect is good, that in the process of solute transport, the concentration of the pollutants reduce conforms to the first-order decay equation, but because of the complexity of the karst water system in the study area and the migration transformation model parameters and to solve the complexity of the result in the accuracy and reliability of the model remains to be improved.

The reduction of pollutant concentration over time in the actual conditions did not reach the extent in the simulation results, because the biochemical reactions of pollutants need to take place under certain conditions. In general, the groundwater environment near the pollution center can provide this condition, so it is more prone to biodegradation reaction. However, the groundwater flow along the groundwater is more complex, and the groundwater environment changes with the change of seasons, so the reduction and dechlorination reaction of pollutants are limited. In addition, changes in the underground water flow field will also lead to changes in the concentration field of chlorinated hydrocarbons when pumping a
large amount of water for a long time. Therefore, there is a certain error between the simulated value and the measured value. According to the predicted results, although the degree of carbon tetrachloride pollution in karst water is reduced, especially in the middle of the pollution plume, the carbon tetrachloride pollution in karst water is still widespread, and the chlorinated hydrocarbon pollution in karst water still poses a great threat to human health in the coming decades.

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