Study on the Law of Carbon Tetrachloride Migration in Groundwater System

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Abstract. Carbon tetrachloride (CCl₄) has a lot of toxic effects on the human body. According to our survey, the pollution of carbon tetrachloride in groundwater in the eastern part of Jinan City is serious. In this study, 40 sampling points were selected in the study area of 100km², and carbon tetrachloride was detected in all sampling. The highest sampling point concentration as high as 20.87 µg / L. The concentration of carbon tetrachloride detected in 40 sampling points ranged from 1.68 to 20.87 µg / L, and most of them exceeded the standard value of 2 µg / L. In order to control the carbon tetrachloride pollution, a solute transport model was established by GMS software to predict the carbon tetrachloride pollution in the study area in the next 15 years. The results show that the concentration of carbon tetrachloride in the groundwater system will decrease to a certain extent, but there is still a considerable distance from the national standard, and the pollutants have tendency to migrate to the southeast and northwest.

Introduction

Carbon tetrachloride is a kind of chlorinated hydrocarbons, which has been widely used in industry in recent years. Groundwater environment deterioration has become one of the serious environmental pollution problems in China [1,2]. CCl₄ can cause a harm to human liver, so the pollution control is necessary. Domestic and international research about the pollution and migration of carbon tetrachloride have been done at present, but the related research mainly focuses on laboratory simulation [3-5].

The study area, 10km away from the urban area, is about 100km². We screen 40 sampling points from 85 monitoring points. This research detected carbon tetrachloride in all sampling points, 39 of which exceeded the national pollution standard. This paper will draw the pollution profile by using the carbon tetrachloride concentration values at each sampling point. The main parameters (dispersion coefficient, retardation coefficient, adsorption and degradation coefficient) of solute transport and transformation were obtained by sand column dynamic simulation experiment. The solute transport model will be established to predict the pollution of carbon tetrachloride in the region 15 years later by using the GMS. The study of the migration regularity of pollutants in groundwater is very meaningful to groundwater pollution control [6].

Spatial Distribution Characteristics of Carbon Tetrachloride Pollution

The study area has a total of 85 monitoring points, select 40 of them to take groundwater samples. The concentration of carbon tetrachloride in the sample was analyzed by GC / MS. Gas chromatography / mass spectrometry chose Fingan MAT MS-DS4510. According to the test results, carbon tetrachloride concentration distribution shown in Figure 1. It can be seen from the figure that the northeastern part of the study area is seriously polluted. The area where the pollution is excessive are mainly concentrated in the BQ, PJY and LSG village. The concentration of sampling points near BQ is as high as 20.87 µg / L, and the concentration near LIZ was reduced to 14.52 µg / L. The lowest concentration is No. 30 sampling point which is 1.68 µg / L. There is a chemical plant near BQ, so we speculate that the enterprise is the main source of carbon tetrachloride in the study area.
Dynamic Simulation of Carbon Tetrachloride

Experimental Materials

The sand column materials used in the experiment were taken in the field of the study area. The grading of gravel particles equal to the fissure rate of the karst fissure medium in the groundwater system is formulated. The gravel was air-dried and then loaded into three experimental simulations. Configuration parameters are shown as Table 1.

<table>
<thead>
<tr>
<th>dry weight g/cm³</th>
<th>specific gravity g/cm³</th>
<th>porosity</th>
<th>Permeability coefficient m/d</th>
<th>Organic matter content</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.86</td>
<td>2.56</td>
<td>39.28%</td>
<td>40.17</td>
<td>0.00098</td>
</tr>
</tbody>
</table>

Quartz glass was used as experimental sand column in the experiment. The length of the quartz glass column is 1 m and the inner diameter is 15 cm. Each glass column has 4 sampling holes, and the distance between every single hole is 2 cm. Mixed 5 kg sand and 600 ml water, and then put them into three quartz columns. Three quartz columns numbered A, B and C were used for three sets of experiments, respectively. In the sand column of the inlet and outlet filled with large particles of quartz sand and copper fine mesh to prevent the loss of sand. The average velocity of the groundwater flow in the study area is 12.68 m/d. Adjust the peristaltic pump to make the experimental water flow consistent with natural conditions. Experimental device diagram shown in Figure 2.

Figure 1. Concentration distribution of carbon tetrachloride.

Figure 2. Experiment device diagram.
Experiment Procedure
In order to obtain the main parameters of solute transport and transformation, a total of three experiments were designed to obtain the dispersion coefficient, the resistance factor and the degradation coefficient respectively.

Trace Experiment
Before the start of the experiment, rinse the experimental column with distilled water for 36 hours to remove any salt that may be contained in the sand. In the experiment, the concentration of 0.1 mol/L NaCl solution was continuously input with peristaltic pump. The chloride ion concentration of each sampling point was measured regularly, and the experiment was stopped until the chloride ion concentration of each sampling point is stable.

Migration Transformation Simulation Experiment
The principle of carbon tetrachloride migration and transformation is the same as that of trace experiment. The concentration of 15 mg/L CCl₄ solution was continuously input with peristaltic pump. The carbon tetrachloride concentration at each sampling point was measured at regular intervals and plotted as a concentration diachronic curve to simulate the change in the concentration of carbon tetrachloride in different time and space conditions.

Simulation Experiments of Adsorption and Degradation
Organic pollutants in the aquifer can be adsorbed by soil particles and can also be degraded by microorganisms present in the aquifer. The degradation products of carbon tetrachloride are chloroform. The purpose of this experiment is to understand the adsorption and degradation of carbon tetrachloride in nature. The concentration of 15 mg/L CCl₄ solution was continuously input with peristaltic pump. We observed the changes in the concentration of chloroform and carbon tetrachloride degradation products in the tail bottle and draw the density diachronic curve.

Experimental Results
The dispersion coefficient of the study area is 10.2 m²/d in the horizontal direction and 3.3 m²/d in the longitudinal direction. The retardation factor is 6.85. The adsorption coefficient is 4.3 × 10⁻⁵, and the degradation coefficient is 0.0013/d.

Numerical Simulation of Transfer and Transformation of Carbon Tetrachloride

Generalization of Hydrogeological Conditions
The assumption of boundary condition needs to understand the geological conditions of water temperature in the research area [7]. The southern part of the study area is low hills and the groundwater is supplied by groundwater runoff, which is defined as constant flow boundary. The northern part of the study area is a cross zone in limestone and clastic. Deep groundwater is blocked from the north movement channel and excreted to the surface in the form of spring water. The amount of excretion is approximately equal to the amount of recharge minus the amount of excretion, so the northern boundary of the study area is generalized as a constant flow boundary. The contour of groundwater table in the east and west are generally perpendicular to the boundaries of the study area, which is generalized as zero flux boundaries. The aquifer is covered with impermeable Quaternary clay layer, so infiltration of atmospheric precipitation has little effect on deep water and can be neglected, so the upper boundary is generalized to the confining boundary. The lower part of the aquifer is impermeable rock formation, so it is defined as the confining boundary. Deep groundwater mainly occurs in Ordovician limestone, which lithological conditions are single, so the aquifer medium is generalized to homogeneous aquatic media. Because of the horizontal scale of the study area is much larger than its vertical dimension in the vertical direction, the groundwater is generalized to an unsteady flow on a two-dimensional dimension.
Parameter Partition

According to the lithology data of the study area, the study area is divided into three parameter zones, which is shown as Figure 3.

![Parameter partition drawing](image)

Figure 3. Parameter partition drawing.

The model is identified based on existing groundwater level observations. The observation data of the existing groundwater level in the study area is the water level observation in 2014. The parameters of the water flow model are shown in Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter area 1</th>
<th>Parameter area 2</th>
<th>Parameter area 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific yield</td>
<td>0.23</td>
<td>0.23</td>
<td>0.28</td>
</tr>
<tr>
<td>Permeability</td>
<td>34.56</td>
<td>43.20</td>
<td>51.84</td>
</tr>
<tr>
<td>Coefficient m/d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity</td>
<td>42%</td>
<td>34%</td>
<td>31%</td>
</tr>
</tbody>
</table>

Simulation Results and Analysis

The results of the first survey were taken as the initial values, and the change of the concentration of carbon tetrachloride in the aquifer was simulated. Part of the simulation results are shown in Figure 4.

![Simulation results](image)

Figure 4. Results of simulation.
It can be seen from the above figure that the trend of the observed value curve and the calculated value curve is basically the same during the simulation period, so the model established in this study can basically reflect the migration and transformation of carbon tetrachloride in the study area. The observed curve has a first rise and fall after the phenomenon, but the range is not great. The speculation may be due to changes in the seasonal or temperature of the study area, resulting in changes of the groundwater system in the redox conditions. The model can basically reflect the migration and transformation of carbon tetrachloride in the study area. This study used this model to predict the concentration of pollutants in groundwater systems in the next 10 to 15 years. The forecast results are shown in Figure 5-7:

Figure 5. Contest map of carbon tetrachloride concentration in the study area in 2016.

Figure 6. Contest map of carbon tetrachloride concentration in the study area in 2020.

Figure 7. Contest map of carbon tetrachloride concentration in the study area in 2024.
It can be seen from the figure that in the next 15 years the concentration of carbon tetrachloride in the groundwater system in the study area will be reduced to a certain extent, but there is still a considerable distance from the national standard. The concentration of carbon tetrachloride in the two monitoring areas of HXCL and ZD showed a decreasing trend, and the average concentration of carbon tetrachloride in the two monitoring areas decreased by 5% and 3% respectively in the next 10 years. The pollutants have a tendency to migrate to the southeast and northwest, which is consistent with the groundwater flow in the area.

Conclusion
(1) All 40 samples were detected carbon tetrachloride in the study area and 39 concentrations exceeded the national standard. Local groundwater carbon tetrachloride is seriously polluted and needs to be treated in time.
(2) Three groups of experiments were designed in this research to determine the influence factors of the aquifer media on the migration and transformation of carbon tetrachloride in the study area.
(3) The dispersion coefficient was determined by the tracer experiment of chloride ion. The retardation factor was obtained by the migration and transformation experiment of carbon tetrachloride. The adsorption coefficient and the degradation coefficient were obtained by adsorption and degradation simulation experiments.
(3) In this study, the mathematical model of groundwater flow and the model of solute transport and transformation were established. The parameters were adjusted and verified. The established model was basically consistent with the measured data, which could reflect the groundwater flow condition. According to the simulation results, the concentration of carbon tetrachloride in the groundwater system in the study area will be reduced to a certain extent in next 15 years, but there is still a considerable distance from the national standard.

Acknowledgement
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Reference