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Carbon tetrachloride pollution pathway of groundwater a typical contaminated site in the east of the city

P Jiang1,2, Z M Ma1,2,4, W W Yu3 and M Wen1,2

1School of Resources and Environment, University of Jinan, Jinan 250022, China
2Research Center of Groundwater Numerical Simulation and Pollution Control Engineering in Shandong Province, Jinan 250022, China
3Best Justicial Testing Technology (Qing Dao) Co., Ltd, Qingdao 266500, China
E-mail: stu_mazm@ujn.edu.cn

Abstract. Determine 40 sampling points basing on a comprehensive monitoring. Determine the spatial distribution characteristics of the carbon tetrachloride by using the software of ArcGIS. Determine the location of the pollution sources by using MT3DMS program and Hook-Jeeves arithmetic to simulate, and connecting with the actual situation of carbon tetrachloride to analyze pollution causes. The results show that the source of carbon tetrachloride is located in the northeast near a chemical plant in the study area, whose pollutant concentration is diminishing from northeast to southwest. The main reasons to the pollution are that factories discharge waste water at random, leakage of open channel and culvert, sewage irrigation and the vulnerability of geological conditions in this area.

1. Introduction
The production and use of CCl4 (carbon tetrachloride) is the main source of CCl4 pollution of groundwater environment. Groundwater contamination with carbon tetrachloride was common in the industrial complexes [1, 2]. It is commonly found in groundwater and surface water at concentrations exceeding the maximum contaminant level of 5 μg/L [3, 4]. Carbon tetrachloride data from Cape Grim and other strategic sites around the globe have been used to derive global and regional CCl4 emissions (Asia, about 75% of global emissions; Africa about 10%; North and South America about 10%; Europe about 5%; Australia and New Zealand lest than 1%) [5]. China's contribution to global emissions increases from 7.5% to 19.5% during 1992–2009, but the contribution is reduced to 9.9% and 8.0% in 2010 and 2011 [6]. The shallow groundwater along the Xiaoqing River in Shandong Province has been polluted by CCl4 with a maximum concentration of 380 μg/L and a pollution area of 80 km² [7], based on the investigation and every day monitoring data of the CCl4 pollution in the groundwater. The contaminated area at the initial stage reached the max contaminant concentration of 249.7 μg/L [8]. Jiangsu Xuzhou, Shandong Zoucheng, Hebei Handan, Beijing suburbs and other areas have found groundwater CCl4 pollution phenomenon [9]. Through an analysis of shallow groundwater in a certain area show that the detection rate of CCl4 was 26% in May 2000, 32.5% in December 2000, in May 2001 was 58.06%, 32.69% in July 2001 [10].

Groundwater pollution source identification problem is the inverse problem of the groundwater and optimization method is the best method for solving this problem [11]. The commonly used optimization methods have Newton Method, Simplex Method, Conjugate Gradient Method, Hooke-Jeeves Method, Genetic Algorithm and Simulated Annealing [12]. Ayvaz used Harmony
Search Algorithm to invert the location and intensity of groundwater pollution source [13]. Ayyaz used a new simulation–optimization approach where a binary genetic algorithm and a generalized reduced gradient method are mutually used that is proposed for solving the areal groundwater pollution source identification problems [14]. Mirghani used Parallel Evolutionary Algorithm to identify groundwater pollution source [15]. Jiang Simin made use of Hybrid Hook-Jeeves and Attractive Repulsive Particle Swarm Optimization Method, combining MT3DMS program, to invert the location and intensity of groundwater pollution source [16]. Bashi-Azghadi presents a new regret-based optimization model which can rapidly identify an unknown pollution source [17]. Jiang Simin adopted Hybrid Simplex Method of Simulated Annealing to calculate the intensity of groundwater source [18]. Datta presents a new source identification methodology that uses a classical nonlinear optimization model linked to a flow and transport simulation model [19].

Karst water samples sampled at 40 monitoring sites will be analyzed to find out the characteristic of groundwater CCl₄ pollution. Groundwater CCl₄ pollution source identification model will be build, which will be simulate through using MT3DMS program and Hook-Jeeves arithmetic to identify pollution sources. Thinking about pollution sources of CCl₄, hydrogeological condition and pollution way of CCl₄, causes of groundwater CCl₄ pollution will be analyzed.

The study area located in the east of the city with a total area about 120 km². Study area belongs to the warm temperate continental monsoon climate. The study area has obvious seasonal precipitation, the average rainfall 660.3mm for many years, more concentrated in the summer months of June to September, accounting for 75% of total annual precipitation. The annual evaporation of study area is 1717.5 mm, which is 2.6 times of the annual precipitation, the month of evaporation of the largest amount is July, the average evaporation is up to 254.8 mm. The formation of a specific area of hydrogeological conditions and distribution will be affected by climate, regional geological structure, stratum lithology, topography factors and other factors, which the geological structure is the decisive factor. The main types of groundwater are loose rock pore water and fracture-karst water in the study area. The study area is located in the north of mountai block uplift, which belongs to the category of luxi vortex structure system on the geological structure, relatively complete formation development. The formation from south to north from the old to the new is outcrops of Cambrian, Ordovician, Carboniferous-Permian, Mesozoic and Cenozoic Quaternary, Yanshanian igneous rock. Loose rock types of pore water in the study area are mainly distributed in northern piedmont inclined plain to the Yellow River alluvial plain, covering most of the area in the study area of quaternary strata thickness increases gradually from south to north, whose thickness range between 20 to 120 m. Fissure karst water in the study area are mainly distributed in the south of the study area of low hilly land and buried deep under Quaternary pore water aquifer. The depth of shallow ground water in the study area is in commonly 7 meters to 30 meters. The recharge of shallow groundwater mainly comes from atmospheric precipitation in the south. The main supply sources of shallow groundwater in northern of the study area is the recharge of deep groundwater in addition to the atmospheric precipitation and surface infiltration recharge rivers. A large number of shallow groundwater in the study area is used in industrial and agricultural production and the supply of spring water. In addition, the rest run off into the Xiaodong River.

2. Methods

2.1. Data source
In view of the hydrogeological conditions in the studied area and the distribution characteristics of different enterprises, the sampling points are arranged as follows: make the sampling points distribution on all kinds of hydrogeological conditions, in order to reduce the unnecessary loss because of the concentrated distribution of the sample points; try best to make sure all kinds of industrial waste water pollution of groundwater can be analyzed. According to the above principles of sampling point arrangement, there are 40 different sample points in the studied area as shown in figure 1.
Figure 1. The sample points in the study area.

2.2. Distribution characteristics
Based on the China national standard method and the EPA method, GC/MS method was used to analyze the concentration of CCl\textsubscript{4} to each sample. Get the detection rate and exceeding rate of CCl\textsubscript{4} in the study area as well as the statistical data based on the statistical analysis to the concentration of CCl\textsubscript{4} that is measured. The results show that the detection rate of CCl\textsubscript{4} is 100\%, the exceeding rate is 94.83\%, and the minimum value is 1.50 μg/L, the maximum is 23.31 μg/L. Choose the ordinary kriging method to do the interpolation of the concentration of the pollution that was measured with the software of ArcGIS. The spatial distribution of CCl\textsubscript{4} pollutants in the study area is showed in figure 2.

Figure 2. Space distribution of CCl\textsubscript{4} in the study area.

2.3. Source apportionment
Groundwater pollution source identification problem is the inverse problem of the groundwater and is the inversion of the pollution source location and concentration on the basis of the concentration of CCl\textsubscript{4} at sampling sites. Groundwater pollution source inversion can be converted into solving
optimization model that regards pollution source location and concentration as the decision variables. In the process of solving optimization model, groundwater flow model and groundwater solute migration model need to be solved continually. So, proper groundwater flow model and groundwater solute migration model are the basis of identifying groundwater pollution source. In this paper, MODFLOW and MT3DMS program are selected to simulate groundwater flow model and groundwater solute migration model, respectively.

Groundwater flow equation of MODFLOW:

$$\frac{\partial}{\partial x} (K_x \frac{\partial h}{\partial x}) + \frac{\partial}{\partial y} (K_y \frac{\partial h}{\partial y}) + \frac{\partial}{\partial z} (K_z \frac{\partial h}{\partial z}) + W = \mu \frac{\partial h}{\partial t}$$

(1)

Where, $h$ is groundwater level, $K_x, K_y, K_z$ are hydraulic conductivity in $x, y, z$ direction (m·d⁻¹), $W$ is source and sink (1/d), $\mu$ is specific storage (1/d) and $t$ is time (d).

Groundwater solute transport equation of MT3DMS:

$$\frac{\partial (\theta c)}{\partial t} = \frac{\partial}{\partial x_i} (\theta D_{ij} \frac{\partial c}{\partial x_j}) - \frac{\partial}{\partial x_i} (\theta v_i c) + q_i c_s$$

(2)

Where, $\theta$ is porosity (dimensionless), $c$ is solute concentration (mg·L⁻¹), $t$ is time (d), $D_{ij}$ is coefficient of dispersion (m²·d⁻¹), $v_i$ is the actual water flow rate (m·d⁻¹), $q_i$ is value of recharge and discharge of unit volume aquifer (m³·d⁻¹) and $c_s$ is solution concentration in source and sink (mg·L⁻¹).

Objective function

$$E(x, y, z, q) = \sqrt{\frac{1}{n_g n_i} \sum_{i=1}^{n_i} \sum_{j=1}^{n_g} \left( c_{i,m}^{\text{f}} - c_{i,g}^{\text{f}} \right)^2}$$

(3)

Where, $c_{i,m}^{\text{f}}$ is value of simulation of monitoring site of i in term of j(mg·L⁻¹), $c_{i,g}^{\text{f}}$ is observed value of monitoring site of i in term of j(mg·L⁻¹), $n_g$ is number of observation well, $n_i$ is number of observation.

2.4. Constraint condition:
Except groundwater flow model and groundwater solute migration model mentioned above, the value range of the location of pollution source and pollution intensity should be taken into account. The value range of the location of pollution source is entering study area and the location of pollution source is expressed in layer, row and column of finite difference grid. So, the coordinate of the location should be integer. The pollution intensity should have upper and lower limit in order to find out proper intensity fast. The pollution intensity isn’t too maximum but also too minimum.

According to above processing, the problem of groundwater pollution source identification will be changed into optimization model. Based on MT3DMS program, using Hybrid Hooke-Jeeves and Attractive Repulsive Particle Swarm Optimization Method [16], the optimization model of groundwater pollution sources will be simulated and calculated.

3. Results and discussion

3.1. Distribution characteristics of CCl₄
As can see from figure 2, the high values area of concentration appears in the northeast of the study area around the sample point 46,47,48,71. And the concentration was decreasing from the center with high value area to the southwest in the study area, low concentration area is concentrated in the study
area in the northwest and south parts. The concentration of CCl₄ near the 48 point is as high as 23.00 μg/L, and near 30 sampling point is only 1.80 μg/L. The standard contamination of CCl₄ in groundwater is 2 μg/L [20]. The concentration of sample that was checked out was 1.50 ~ 23.31 μg/L. The figure shows that the detected value has been exceeded in many areas, and it shows that the pollution of CCl₄ is very serious. The concentration of CCl₄ is as high as 20.87 μg/L near a chemical factory. Thus, it shows that the factory is the main pollution source of CCl₄ in the study area. The highest concentration of CCl₄ is 23.31 μg/L in the study area, which is 11.65 times higher than the standard value. It shows that the pollution of CCl₄ in groundwater is very serious.

3.2. The law of CCl₄ migration
Affecting the groundwater CCl₄ migration mainly factors include convective dispersion, volatilization, adsorption and biodegradation.

Based on the results of the first survey, the change of the concentration of CCl₄ in the aquifers of the study area is simulated and the results are shown in figure 3.

![Figure 3. Simulation value and actual value.](image)

Figure 3 shows that the trends of the observation curve and the calculated curve are basically the same in the simulation. The observed curve rises and falls once after the phenomenon, but the range is not large. The speculation may be due to changes in the season or temperature of the study area, leading to changes in the groundwater system under redox conditions. The model can basically reflect the migration and transformation of CCl₄ in the study area.

3.3. Pollution ways of CCl₄
The position of sources is shown in figure 4. It is consistent with spatial distribution of CCl₄ by ArcGIS, showing a high concentration of northeast and gradually decreasing trend to the southwest. There is a chemical factory near the pollution sources through field visits, which discharged large number of CCl₄ by open channel and culvert. The results show that the chemical factory is the pollution source of CCl₄. Pollution ways of CCl₄ of groundwater in the study area are as follows:

- As important industrial and mining enterprises in the study area, in the process of each enterprise production operation, soils in the upper layer are usually polluted first. Pollutants retention infiltrates through leaching. These contaminants run into the underground through rainfall, resulting in widespread contamination of groundwater.
Research in northern area, the lithology of vadose zone is given priority to with powder sand belt, loose structure, penetration ability is stronger, permeability coefficient is 0.30 ~ 0.35, water depth is general less than 3 m, pollutants directly run into underground or seep into the ground through rainfall. Thus, pollute the groundwater. Moreover, due to the presence of a chemical factory in the northeast of the study area, make the pollution of CCl₄ is most serious nearby. Research in southern area, the lithology of vadose zone is given priority to with sand-loam and cohesive soil gravel, penetration ability is poorer, permeability coefficient is 0.15 ~ 0.20, water depth is general more than 10 m. However, due to the loess with vertical joints, gravel sandwich has some porosity, which leads to poor vulnerability and makes it easy for CCl₄ to infiltrate into ground, pollute groundwater.

The discharge way of sewage of industrial and mining enterprises in the study area is complex, which have open channel and culvert. The sewage ditches are on the top of the normal water level, the bottom is given priority to with clay and silty clay layer, CCl₄ pollutants seep into the vadose zone though ditches, polluting the groundwater. Most of the sewage channels in the study area are in north-south direction, basically consistent with the groundwater flow direction, but some sewage channels are in east- west direction, the drainage ditches transverse cutting of groundwater flow direction and caused more serious groundwater pollution. The closer distance to the channel is, the more serious the pollution is.

Most industrial enterprises in the study area don't have a complete management system, and in all aspects of operation or production process there is a serious phenomenon such as run, drip, and leak. And the pollutant of production of these enterprises is most CCl₄, which is difficult to avoid seeping into groundwater and polluting it. In addition, most of irrigation wells in the study area are scrapped due to the reduction of groundwater level, and the farmers have to refer to enterprises waste water or river water for irrigation. It is easy to cause a large area of groundwater pollution.

4. Conclusion
Determine 40 sampling points basing on a comprehensive monitoring. Determine the spatial distribution characteristics of the CCl₄ by using the software of ArcGIS. Direct supply of atmospheric precipitation and surface water to ground water, complementary relationship between loose rock pore water and fracture-karst water all lead to hydrogeological conditions vulnerable in the study area, which makes it easy for surface pollutants to infiltrate into ground and thus pollute groundwater. It is
found that through research and analysis, the ability of the aquifer to remove CCl₄ is not prominent. By analyzing industrial layout and hydrogeological conditions, there are mainly two causes of carbon tetrachloride pollution: the vulnerability of geological conditions in this area; the other being the serious pollution in this area caused by remaining pollution sources of the industrial.

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