Genesis analysis of karst water trichloroethylene pollution in the east of a city

Peng Jiang1,2, Zhenmin Ma1,2,* and Ming Wen1,2
1 School of resources and environment, University of Jinan, Jinan 250022, China
2 Research center of groundwater numerical simulation and pollution control engineering in Shandong province, Jinan 250022, China
*corresponding author’s e-mail: stu_mazm@ujn.edu.cn

Abstract. To understand the situation of Karst water Trichloroethylene (TCE) pollution in the east of city, Karst water samples sampled at 43 monitoring sites were analyzed. Result shows that relevance ratio of TCE is 100%, over the standard rate of 97.67% and the maximum value is 73.64μg/L, as 14.73 times as the standard value(5μg/L). Causes of groundwater TCE pollution were analyzed. Result shows that indiscriminate discharge of waste water and poor groundwater vulnerability are the main reasons. And based on the reasons, the pollution ways of TCE were found out.

1. Introduction
TCE is mainly used to clean metal, extract solvent, chemical materials, dry cleaning, and so on. In recent years, TCE is widely used to electrical and mechanical industry, clean metal parts and electronic components[1-3]. With the widely application of TCE, groundwater TCE pollution problem has become more serious. In groundwater pollution investigation of America, the relevance ratio of TCE was the highest, as much as 36%,[4,5]. In 1970s, TCE was found in groundwater and in the latest investigation, groundwater TCE pollution was more serious[6]. TCE was found in groundwater of Germany, Britain and Italy[7-9]. In China, TCE was found in groundwater, too. In groundwater organic contamination investigation of Taihu watershed, at 36 monitoring sites, the relevance ratio was 30.6% and serious pollution area fit into the industrial distribution[10].

Karst water samples sampled at 43 monitoring sites will be analyzed to find out the characteristic of groundwater TCE pollution. Thinking about pollution sources of TCE, hydrogeological condition and pollution ways of TCE, causes of groundwater TCE pollution will be analyzed.

2. Materials and methods
2.1 Study area
Study area is located in the east suburb of a city, between the Taishan mountain area to the south and alluvial plain of Yellow River to the north, low-lying north south high and low-lying west east high. From south to north, geomorphic type is low hills denudation zone, piedmont clinoplain and alluvial plain of Yellow River. The climate belongs to warm temperate continental monsoon climate, with four different seasons, the rainfall in summer is more than that in winter. Average annual precipitation is 660.3mm. The mainly rainfall focus on July to September.

The distribution of the Quaternary unconsolidated strata is uneven in study area and Quaternary unconsolidated strata is mainly distributed in piedmont clinoplain and alluvial plain of Yellow River, thickness increasing gradually from south to north. Quaternary unconsolidated strata is divided into
two layers. The upper layer is brown loam layer mixed with gravel and dinas, even and widely distributed, having good permeability. The under layer is purple clay, dense structure, having poor permeability, which is regarded as water-resisting layer. Ordovician limestone is widely distributed in study area. Ordovician limestone is exposed in the south of study area and becomes concealed to the north. The Carboniferous, Permian strata and Magmatic rock are distributed in the north of study area, which are regarded as confining boundary because of its poor permeability. Groundwater system mainly include the karst fissure water system and the loose Quaternary pore water system. Shallow pore water mainly lies in brown loam layer, mainly recharged by atmospheric precipitation, which is the main source of agricultural production. Karst water lies in Ordovician limestone, mainly recharged by atmospheric precipitation in uncover limestone area and also recharged by shallow pore water, which is main water aquifer.

Study area is heavy industrial district. Under extensive Mode of development, groundwater over-exploitation has made groundwater level continual lowering, forming landing funnel of groundwater. Waste water produced in the progress of enterprise production discharges into surface water without wastewater treatment, which makes surface water contaminative. Polluted surface water infiltrating into underground can contaminate groundwater.

2.2 Sampling and analysis
Thinking about the hydrogeological conditions and the distribution characteristics of different plants in study area, 43 sampling sites are set in study area and the layer of sampling is Ordovician limestone(Figure 1).

![Fig. 1 The location of 43 sampling sites.](image)

Because of the concentration of TCE in groundwater is low, mostly in ppb level. Based on National Standard Method and the U.S. Environment Protection Agency (EPA) method, the concentration of TCE in groundwater are analyzed by GC/MS (gas chromatography/mass spectrum) method.

2.3 Methods

2.3.1 Groundwater pollution characteristics. Groundwater pollution characteristics is analyzed based on the map of the distribution of contaminant. The map of distribution can show the shape of pollution, migration tendency, the maximum and minimum of contaminant and the area between a concentration value and another concentration value. On the basis of the concentration of TCE at
sampling sites, firstly, sampling data is dispersed using Kring in mapgis. Secondly, the map of the distribution of TCE in groundwater is drawn through Grid model in mapgis.

2.3.2 Genesis analysis of groundwater TCE pollution. Genesis analysis of groundwater pollution is the process of determining pollution sources, finding out pollution way and analyzing controlling factors. On the basis of determining pollution sources, understanding the permeability of surface oil and the thickness of unsaturated zone is necessary, which determines that contaminants go into underground easily or difficulty. Determining the recharge and discharge correlation between shallow groundwater and surface water and determining whether the recharge and discharge correlation between shallow groundwater and deep groundwater are important. Water is the carrier of contaminants migration. Knowing moving path of all kinds of water in the vertical direction is useful to know the pollution way.

3. Results and discussion

3.1 Groundwater pollution characteristic of TCE

The concentration of TCE at 43 monitoring sites were reported in table 1. From (table 1)we could see that TCE were checked out at all monitoring sites. Among them, the maximum was 73.64μg/L and the minimum was 2.24μg/L. The mean value was 53.37μg/L. Taking EPA drinking water standard(5.00μg/L) as a standard, except monitoring site of 30(2.24μg/L), the concentration of TCE at other sites all exceeded the standard. The rate of exceeding the standard was 97.67% and the maximum was 14.73 times as much as the standard.

| N  | C   | N  | C   | N  | C   | N  | C   | N  | C   |
|----|-----|----|-----|----|-----|----|-----|----|-----|
| 1  | 23.53 | 35 | 39.48 | 71 | 29.66 | 48 | 22.61 | 85 | 43.44 |
| 2  | 44.67 | 36 | 66.54 | 72 | 65.42 | 49 | 69.48 | 72 | 65.43 |
| 5  | 42.11 | 64 | 23.88 | 58 | 70.88 | 50 | 68.87 | 48 | 23.54 |
| 12 | 70.67 | 85 | 43.33 | 73 | 71.22 | 56 | 72.55 |
| 19 | 73.64 | 43 | 30.11 | 74 | 70.26 | 62 | 72.62 |
| 22 | 66.76 | 44 | 30.11 | 75 | 70.34 | 70 | 72.61 |
| 30 | 2.24  | 45 | 29.54 | 77 | 70.22 | 81 | 73.10 |
| 31 | 41.50 | 46 | 28.56 | 78 | 71.35 | 82 | 73.11 |
| 32 | 41.07 | 47 | 27.43 | 79 | 70.33 | 83 | 73.36 |
| 33 | 42.32 | 55 | 65.56 | 80 | 68.76 | 84 | 72.32 |

N: the number of monitoring sites; C: the concentration of TCE at monitoring site.

The map of the distribution of groundwater TCE pollution was drawn by Mapgis, as shown in (Figure 2). It can be seen from (Figure 2) that high concentration of TCE distribute in the middle of study area, around the monitoring sites of 36, 50, 80 and 83, whose shape was dumbbell-shaped. Centering on the area of high concentration, TCE spread around with the concentration of TCE diminished gradually. The area of low concentration distributed in the south of study area.
3.2 Genesis analysis of groundwater TCE pollution

3.2.1 Groundwater TCE pollution sources. The investigation result shows that there are three pollution sources, s-1, s-2 and s-3 in study area, which are shown in Figure 3. It can be seen from (Figure 3) that the three pollution sources are a zonal distribution. The distribution of pollution sources is similar to the distribution of high concentration of TCE in groundwater and the monitoring sites of checking out high concentration of TCE. They are near the pollution sources.
selected, which are mechanical and electrical industries. TCE is used for cleaning metal parts and electronic components in the production process of the ten industries. So, in waster water discharged by the ten industries, TCE is checked out. Among the ten industries, there are three industries discharging waster water to s-1, three industries discharging waster water to s-2 and four industries discharging waster water to s-3.

3.2.2 Poor antifouling property of site aquifer. The buried features of groundwater can decide that contaminants go into underground easily or difficultly. In study area, the lithology of aeration zone is brown loam. The thickness of aeration zone is less than 10m and the hydraulic conductivity of aeration zone is $1.3 \times 10^3 \text{cm/s}$. Good permeability and short migration path result in contaminants going into underground easily. So, it is easy for shallow pore water to be contaminated. There is purple clay layer existing between shallow pore water and Karst water. The thickness of purple clay layer is between 30m and 40m. It has poor permeability, whose permeability is less than $1.3 \times 10^6 \text{cm/s}$. Because of poor permeability and wide distribution, this layer is regarded as water-resisting layer. And, under the natural state, the water table of Karst water is higher than shallow pore water. So, even if shallow pore water is contaminated, Karst water isn’t affected. However, over-exploitation of Karst water makes water table of Karst water decline, forming groundwater depression cone and the water table of Karst is lower than shallow pore. And pumping well casing has been broken because of lacking of repair for long years. For the two reasons given above, shallow pore water supplies Karst water. If shallow pore water is contaminated, Karst water is also contaminated. Therefore, antifouling property of Karst water is poor.

3.2.3 Groundwater pollution way of TCE. Water is the carrier of the migration of contaminants. So, research on groundwater pollution ways of TCE, recharge, runoff and discharge of groundwater need to be found out. Types of groundwater in the study area include shallow pore water and Karst water. Shallow pore water is recharged by precipitation, surface water and the lateral flow. The ways of shallow pore water discharge are artificial discharge, lateral flow discharge and recharging Karst water. Karst water is recharged by the lateral flow and shallow pore water. The ways of Karst water discharge are artificial discharge and lateral flow discharge. It can be seen from Figure 2 that the concentration of TCE in groundwater is very low in the south of study area. So, TCE doesn’t come from the lateral flow, but comes from vertical infiltration of surface pollution sources.

Waster water produced by industries discharged into channels through blow-off line without waster water treatment. Because of channel bottom without seepage prevention, waster water including TCE permeated into aeration zone. Due to good permeability aeration zone, waster water permeated into shallow pore water further to contaminate shallow pore water. When shallow pore water recharged Karst water along the damaged wall of a well, TCE also went into Karst water to contaminate Karst water. In addition, density of TCE is bigger than water and TCE is easy volatile. Insoluble TCE gathered at the bottom of the Karst aquifer and contaminated Karst water by volatilization.

4. Conclusions
The rate of exceeding the standard is 97.67% and the maximum is 14.73 times as much as the standard. The shape of high concentration of TCE is dumbbell-shaped. Centering on the area of high concentration, TCE spread around with the concentration of TCE diminished gradually.

The investigation result shows that there are three pollution sources in study area, waste water outfalls of ten mechanical and electrical industries.

Antifouling property of groundwater is poor. TCE passes through aeration zone and shallow pore water to contaminate Karst water.

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