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Research Article

Characteristics, Distribution, and Source Analysis of the Main Persistent Toxic Substances in Karst Groundwater at Jinan in North China

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Karst water in northern China is an important water source for economic and social development in its distribution area and water source for ecological function guarantee. With the enhancement of human activities, the water quality of karst water in the north has deteriorated and the bearing capacity of economic activities and social and ecological environment has weakened. The study on the distribution characteristics and source analysis of toxic substances in typical karst springs in northern China is of great practical significance for the sustainable development of karst areas in northern China. Based on the abundant karst water samples, the concentration, detection, and spatial distribution of toxic heavy metals and typical organic substances in karst waters were analyzed, the quality was evaluated, and the source of substances was analyzed. The results show that the toxic substances in karst water in Jinan are mainly distributed in the northern part of the Jinan urban karst water subsystem and Baiquan karst water subsystem in Jinan city, and the detection rate is low in other areas. The main distribution areas of toxic substances in karst water are the northeast and southwest parts of Jinan city. In the recharge area and runoff area of the karst spring area, the contribution rate of toxic substances to the comprehensive quality evaluation of karst water is relatively low and relatively high in the drainage area of the spring area. The organic index contributes more to the comprehensive quality evaluation of karst water. The distribution of toxic substances is related to the historical and current industrial layouts, and industrial discharge or leakage is the primary source of pollutants in karst water. The concentration of toxic substances in karst water has persistence and inheritance. This study enriches the research results on the distribution and sources of toxic substances in typical karst springs in northern China and provides essential data support for scientific understanding of the changes in karst water quality and optimization of water resource management in northern China.

1. Introduction

There are 6.85×10^5 km^2 carbonate rock distribution areas in northern China [1] and 1.09×10^{10} m^3/a of karst water resources [2]. Karst water is an important water source for water supply and ecological function guarantee in northern China [3]. The unique geological and topographic conditions make most karst water in northern China discharged in the form of springs or spring samples [4]. In the past 40 years, a variety of environmental problems have arisen in the karst water system in northern China, such as deterioration of water quality, water cutoff of springs, and water level drop [4]. The development and change of these environmental problems have brought challenges to the management of karst water resources, and scientific research is needed to serve the management, protection, and sustainable utilization of water resources.

Jinan is a typical karst water distribution area in northern China. It is known as "city of springs." There are numerous springs in Jinan, and it has "72 famous springs." Karst groundwater is an indispensable and important resource for industrial and agricultural production and social development

in Jinan [5]. Over the past decades, with the industrialization and urbanization of Jinan, the water resource conditions of Jinan karst water system have changed [6–9], and the water quality has changed significantly [6, 10]. The concentration of toxic substances in karst water, including toxic heavy metals and persistent organic compounds, has increased [11, 12], causing negative effects or potential threats to the ecological environment, economic activities and human health [13]. Therefore, it is of great significance for the development and utilization of karst water resources and ecological environmental protection to analyze the concentration and distribution status of persistent toxic substances in underground water in Jinan karst spring area and find out their pollution sources and influencing factors.

The unique hydrogeological conditions make the groundwater quality in the karst area more sensitive to human activities [14, 15]. Persistent toxic substances have caused different degrees of karst water pollution in the karst distribution areas of the world, such as toxic heavy metals in the karst area of southern China [16–19] and persistent organic substances in Italy [20], Turkey [21], China [22, 23], etc. Liu et al. [18] analyzed the hydrochemistry and distribution characteristics of heavy metals in four typical karst underground rivers in southwest China, including As, Cr^{6+}, and other heavy metals and analyzed the influence of human activities. Dong et al. [24] summarized that polycyclic aromatic hydrocarbons (PAHs) and organochloride pesticides (OCPs) are the main toxic organic compounds detected in groundwater of karst spring area in China, and the toxic organic compounds concentration in karst water is relatively low. In the karst spring area of Jinan area, Gao et al. [11] discussed the trace element concentration and distribution change characteristics of Jinan karst water in high and low water periods, including the analysis of toxic heavy metals like Cr^{6+}. Yang et al. [12] summarized the detection of toxic organic compounds in Jinan urban subsystem of karst spring area in Jinan, pointing out that the detection rate of trichloromethane is high. Xu et al. [23] analyzed the distribution rule of toxic organic compounds in karst water in Jinan, pointing out that the detection rate of toxic organic compounds is high and the concentration is low, and its distribution is controlled by the distribution of industrial enterprises and groundwater field. The above results show that there are still few studies on persistent toxic substances in karst water in northern China, and the scattered results mostly describe the distribution or source of toxic substances from one aspect or one side, and the data used are relatively early, and no systematic research results have been seen at present. In this paper, Jinan spring area, a typical karst spring area in northern China, is selected to study the distribution characteristics and source analysis of persistent toxic substances in groundwater, which can supplement relevant research results and provide data support for scientific understanding of the changes in karst water quality in northern China.

2. Materials and Methods

2.1. Overview of the Study Area. Jinan is located in the mid-latitude inland zone and belongs to the warm temperate continental monsoon climate zone. It has the climatic characteristics of drought-prone spring, hot and rainy summer, and cold and dry winter. The annual average temperature is 14.3°C, the annual average precipitation is 641.68 mm (1956–2012), and the annual average evaporation is 1500–1900 mm [13]. The annual distribution of precipitation in the region is uneven, with the rainy season concentrated in June to September, and the precipitation accounts for more than 70% of the annual precipitation.

Jinan geotectonic division is the Luzhong uplift in the Luxi uplift area of the north China plate, which is generally a northdip monoclinic structure with the Neoarchaean Taishan group as the base and the Paleozoic carbonate rock strata as the main body. In monoclinic structure, several groups of northwest-oriented faults are developed, forming relatively independent monoclinic blocks, and each monoclinic block forms a relatively independent karst water system. This specific geological structure condition in Jinan area controls the spatial distribution of regional aquifers, groundwater movement, water circulation conditions, and water-rich conditions.

The study area includes the Jinan-Changqing karst water system and Mingshui karst water system, in which the former is divided into Changqing-Xiaolipu karst water subsystem, Jinan urban karst water subsystem, and Baiquan karst water subsystem (Figure 1). There is basically no hydraulic connection between Jinan-Changqing karst water system and Mingshui karst water system; there are different degrees of hydraulic connection within Jinan-Changqing karst water system, in which the Changqing-Xiaolipu subsystem and the northern boundary of Jinan urban subsystem present weak permeability, and the northern boundary of Jinan urban subsystem and Baiquan subsystem are closely linked.

The carbonate rock fissure karst aquifer system in the study area is composed of the Sup-Zhangxia Formation ($\epsilon_2 z$) and Upper Cambrian Fengshan Formation and Ordovician ($\epsilon_3 f$-O), and the lithology is dominated by carbonate rocks such as limestone, dolomitic limestone, limestone dolomite, and argillaceous limestone. The karst fissures in each karst water system are developed with good connectivity, which is conducive to the recharge, runoff, and enrichment of groundwater. Groundwater recharge is mainly infiltration recharge of atmospheric precipitation, followed by surface water leakage recharge. The underground runoff generally moves from south to north, northwest, and west along the stratum tendency. In the north, it is blocked by gabbro rock and carboniferous and Permian strata, rises to form springs for drainage, or is discharged by artificial mining.

2.2. Layout of Sampling Points. In order to study the distribution characteristics of toxic substances in karst groundwater in Jinan and to facilitate the analysis of pollutant sources, two principles should be grasped in the layout of sampling sites: one is to cover the surface and grasp the macroscopic distribution of toxic substances; the other is to properly encrypt the layout in key areas and study the

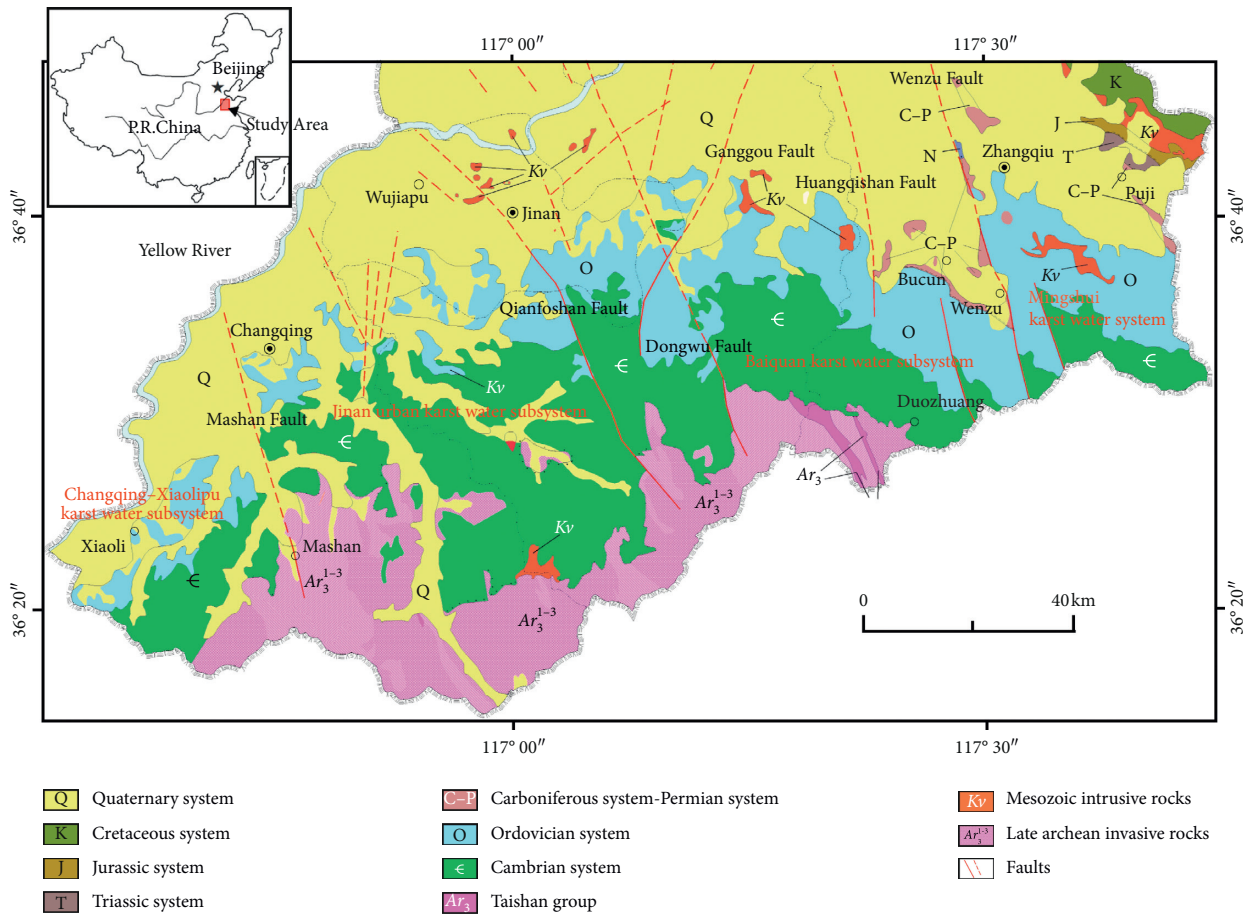

Figure 1: General map of the study area and the division of karst water systems.

distribution characteristics of toxic substances in key areas. A total of 194 sampling points were set up.

2.3. Sample Processing and Determination. Karst water samples were collected at 8.25 on 2011/8/15 and 12.23 on 2012/10/9. Samples were collected and tested in strict accordance with relevant requirements of groundwater quality standard (GB/T 14848-2017). From the recharge area to the drainage area in Jinan karst spring area, samples of karst groundwater were collected along the flow direction of groundwater, and their inorganic hydrochemical and organic components were tested. Groundwater samples are collected directly from the wellhead, the wells are cleaned before collection, and the stored water is discharged from the wellhead. A portable tester was used to test temperature, water temperature, pH value, conductivity, dissolved oxygen, redox potential, and turbidity. When collecting organic samples, the water inflow rate are control without air bubbles and gas flow. Special VOA sample bottles and SVOA sample bottles are sealed and stored and transported in a special refrigerator at 4°C.

2.4. Quality Control and Assurance. Sample determination is controlled by blank method, matrix addition and a parallel sample of matrix addition. The final quantitative results of target test indexes are deducted by blank and corrected by the recovery rate. During the sampling process, 5% parallel samples and 5% outbound samples were collected and standard samples and blank samples were set to track and monitor the sampling and test quality. All organic samples (including experimental samples, blank samples, and spiked samples) were added with recovery indicators to control the efficiency in the sample pretreatment process, and the recovery met the quality control standards as specified in *Technical Requirements for Quality Control of Groundwater Pollution Investigation and Evaluation Sample Analysis* (DD2014-15) by the China Geological Survey. The recovery rates of volatile organic compounds (VOCs) are controlled at 80%~120%, while the recovery rates of semivolatile organic compounds (SVOCs) are controlled at 65%~130%.

2.5. Data Analysis Compounds and Methods. Two-hundred and thirteen samples from all 194 sampling sites were tested for inorganic compounds, including toxic heavy metals, general chemical parameters, and toxic inorganic parameters, and 163 samples from 149 sampling sites were selected for organic component testing. The toxic heavy metals selected in this paper include arsenic, cadmium, hexavalent chromium, lead, and mercury. The general chemical

parameters and the toxic inorganic parameters are determined by traditional analysis methods suitable for karst groundwater [13]. The organic analytes include persistent organic compounds, such as dichlorodiphenyltrichloroethane (DDT). In addition, several typical organic compounds were selected for analysis. The organic compounds include 21 volatile organic compounds, namely, trichloromethane, carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, dichloromethane, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,2-dichloropropane, bromoform, vinyl chloride, 1,1-dichloroethylene, *cis*-1,2-dichloroethylene, chlorobenzene, p-dichlorobenzene, toluene, ethylbenzene, xylene and styrene, 5 semivolatile organic compounds, total benzenehexachloride (BHC), γ-BHC (lindane), total DDT, hexachlorobenzene, and benzo(a) pyrene. The detection limits of the toxic heavy metals and the organic compounds are listed in Tables 1 and 2.

In this paper, the material concentration analysis is carried out by the simple statistical method. The karst water quality evaluation is carried out according to the national groundwater quality standard GB/T 14848-2017, and the spatial distribution characteristics and material sources are analyzed. The substance distribution maps are drawn by the MapGIS software, and the contoured maps are drawn using the method of the inverse distance weighted (IDW). The IDW method mainly depends on the power parameter, and the power parameter used in the paper is 2. The IDW method is a widely used the interpolation method, and its specific calculation processes are no longer repeated in the paper. After the IDW interpolation, the contours are modified manually according to specific hydrogeological conditions to make them more precise.

Table 1: Detection limits of the toxic heavy metals.

No.	Toxic heavy metals	Detection limits (mg/L)
1	Arsenic	0.005
2	Cadmium	0.0002
3	Hexavalent chromium	0.006
4	Lead	0.002
5	Mercury	0.0001

Table 2: Detection limits of the organic compounds.

No.	Organic compounds	Detection limits (μg/L)
1	Trichloromethane	0.1
2	Carbon tetrachloride	0.1
3	1,1,1-Trichloroethane	0.1
4	Trichloroethylene	0.1
5	Tetrachloroethylene	0.1
6	Dichloromethane	0.2
7	1,2-Dichloroethane	0.2
8	1,1,2-Trichloroethane	0.1
9	1,2-Dichloropropane	0.2
10	Bromoform	0.2
11	Vinyl chloride	0.1
12	1,1-Dichloroethylene	0.1
13	*cis*-1,2-Dichloroethylene	0.1
14	Chlorine benzene	0.1
15	Phthalates	0.1
16	Dichlorobenzene	0.1
17	Benzene	0.2
18	Toluene	0.1
19	Ethylbenzene	0.1
20	Ditoluene	0.2
21	Styrene	0.1
22	Total BHC	0.01
23	γ-BHC (lindane)	0.01
24	Total DDT	0.002
25	Hexachlorobenzene	0.01
26	Benzo(a) pyrene	0.002

3. Results

3.1. Concentration and Distribution of Substances

3.1.1. Toxic Heavy Metals. Among the toxic heavy metals, cadmium was detected in 86 samples, the detection rate was 44.3%, and the concentration was 0.0002 mg/L~0.002 mg/L, which were distributed in the whole study area (Figure 2). Lead was detected in 28 samples, the detection rate was 14.4%, and the concentration ranged from 0.002 mg/L~0.007 mg/L, which were distributed in the whole study area too (Figure 3). Hexavalent chromium was detected in 21 samples with a detection rate of 10.8%. Except for the one group located in the south of Jinan spring area with a concentration of 0.48 mg/L, the detection concentration of hexavalent chromium in other samples ranged from 0.006 mg/L to 0.09 mg/L. A group of arsenic was detected with the concentration of 0.0134 mg/L, which was located in the recharge area of the karst water subsystem in Jinan city. Mercury was not detected in all samples.

Overall, the concentration and detection rate of heavy metals in the northwest of the study area along the yellow river and the eastern suburbs of Jinan are relatively low. There are certain detections in a wide area in the south-central and east of the spring area. Samples with a high concentration of heavy metals are scattered around the urban area of Jinan.

3.1.2. Organic Compounds. Among the 149 karst water samples, one or more of the 26 organic compounds were detected in 75 samples and the total detection rate was 50.34%. From the spatial distribution, toxic organic compounds are mainly detected in the karst water subsystem of Jinan urban area and in the north of Baiquan karst water subsystem. Samples with 1 to 3 toxic organic compounds detected were mainly distributed in the southwest of Jinan city and the area from Guodian to Ganggou in the east; samples with 4 or more toxic organic compounds detected were mainly distributed in the area from south industrial road in the eastern suburbs to Wangsheren town, which is the area with the most serious organic pollution of fissure karst water in Jinan city (Figure 4).

The highest detection rate of individual organic compounds was trichloromethane, with a detection rate of

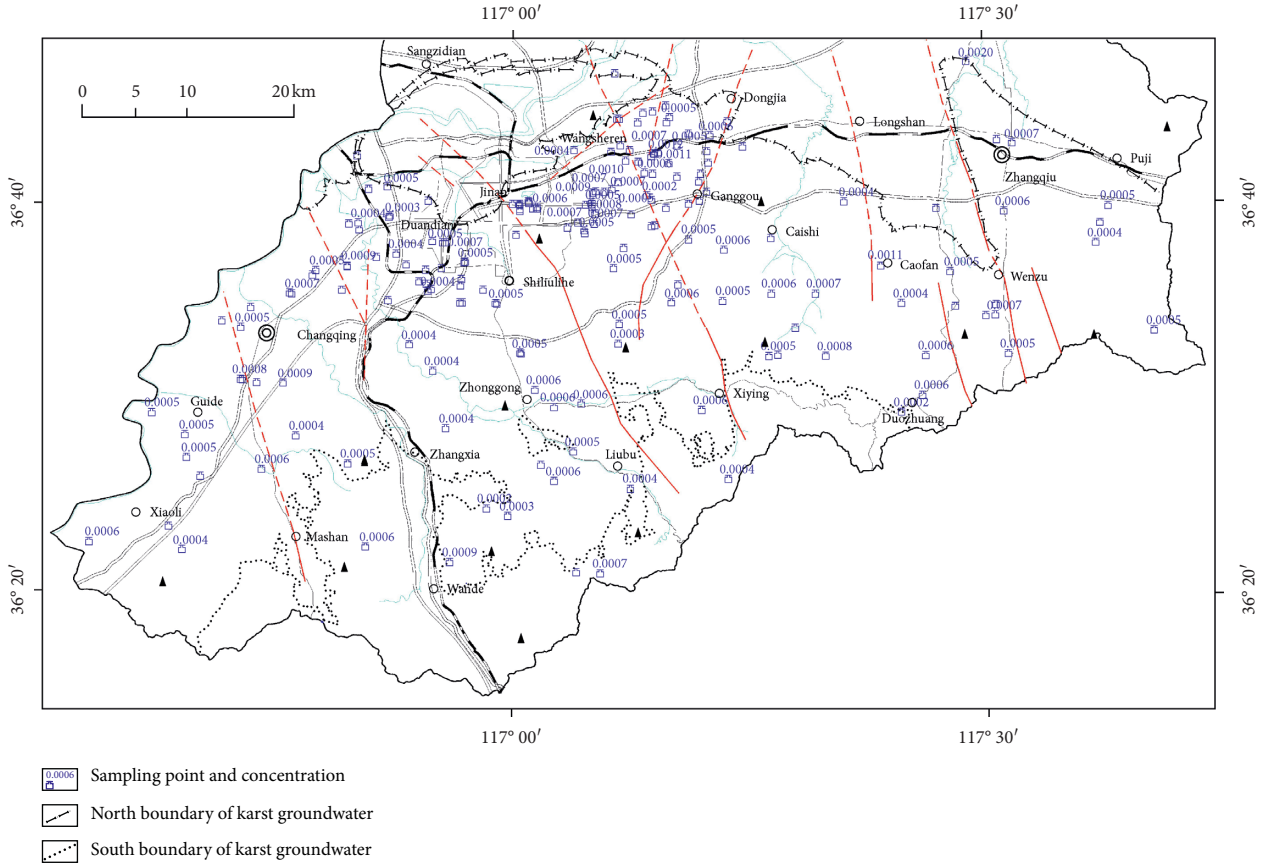

Figure 2: Distribution of Cd concentrations in fractured karst water.

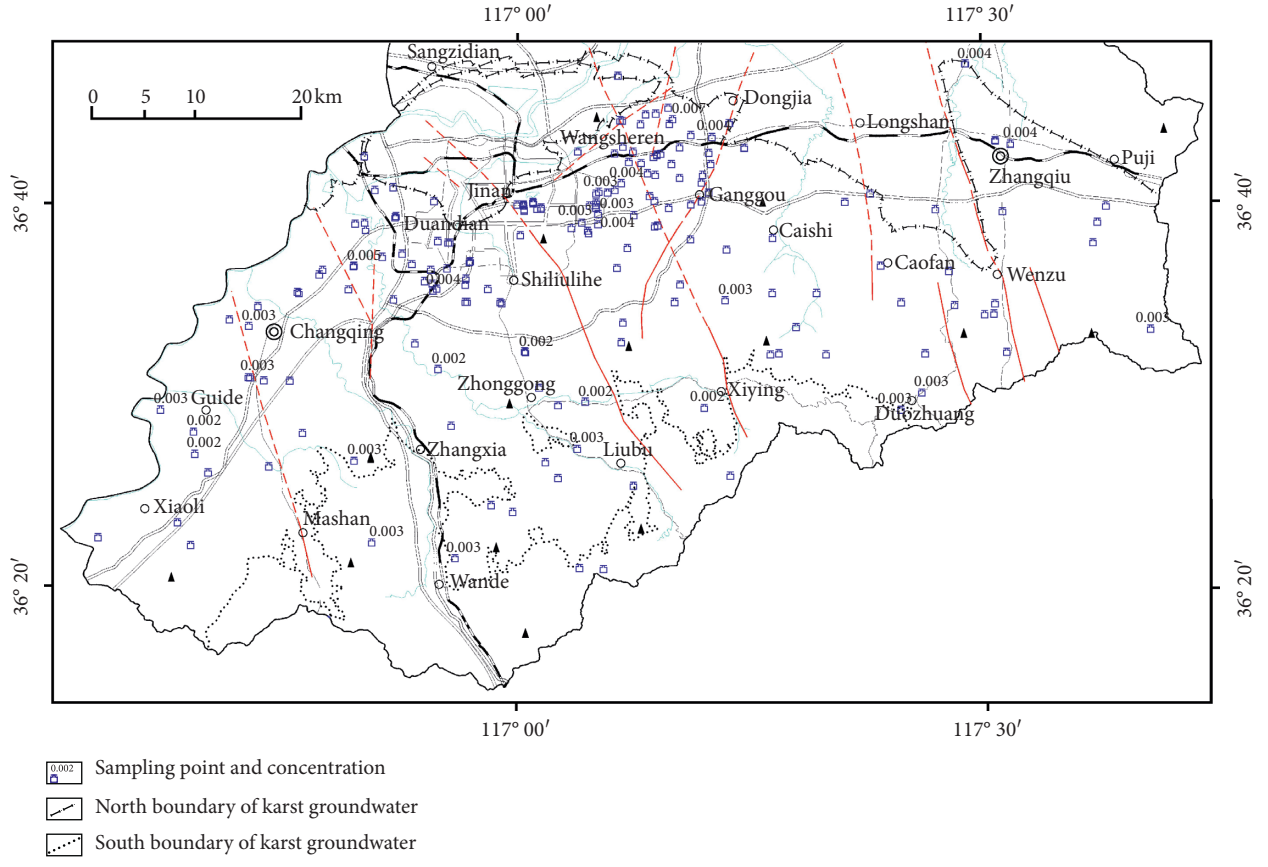

Figure 3: Distribution of Pb concentrations in fractured karst water.

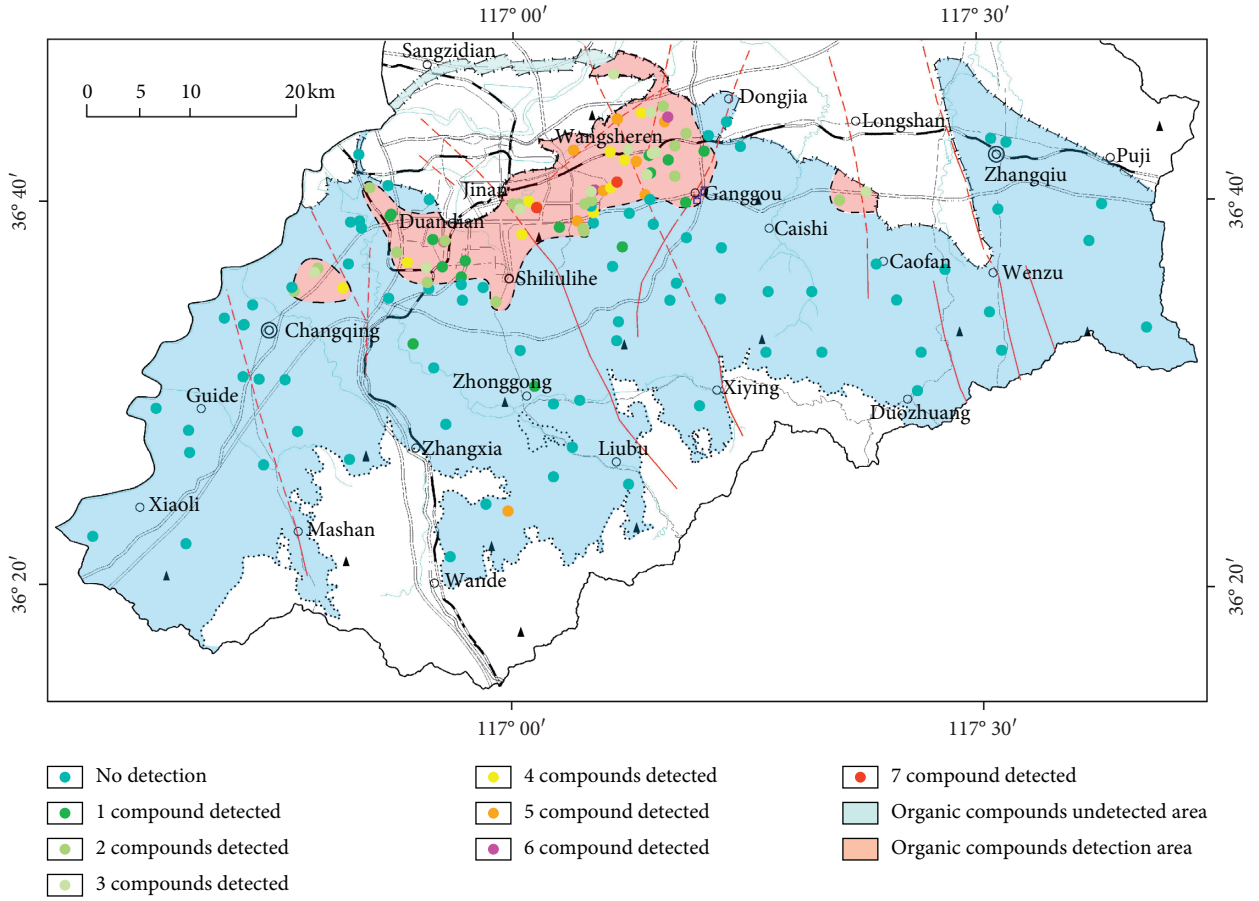

Figure 4: Distribution of the number of toxic organic compounds in fractured karst water.

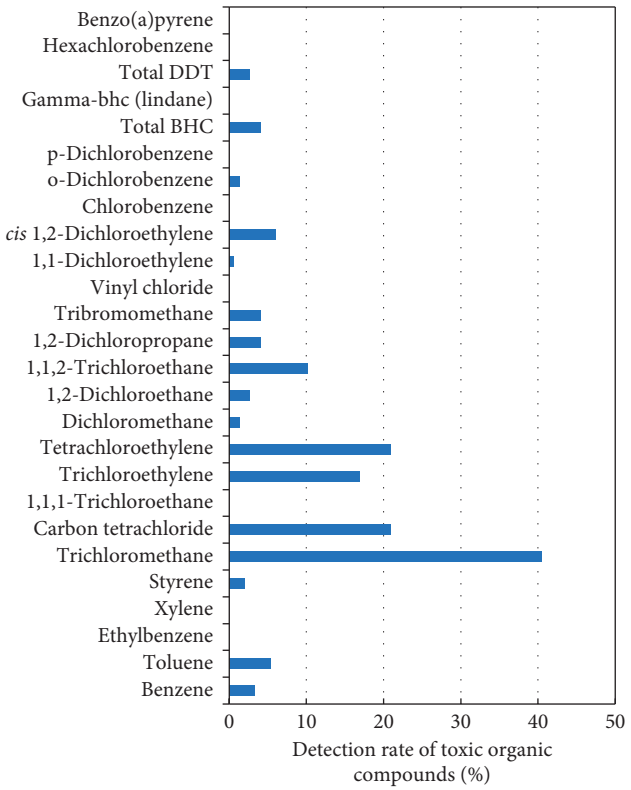

Figure 5: Distribution of toxic organic compound detection rate.

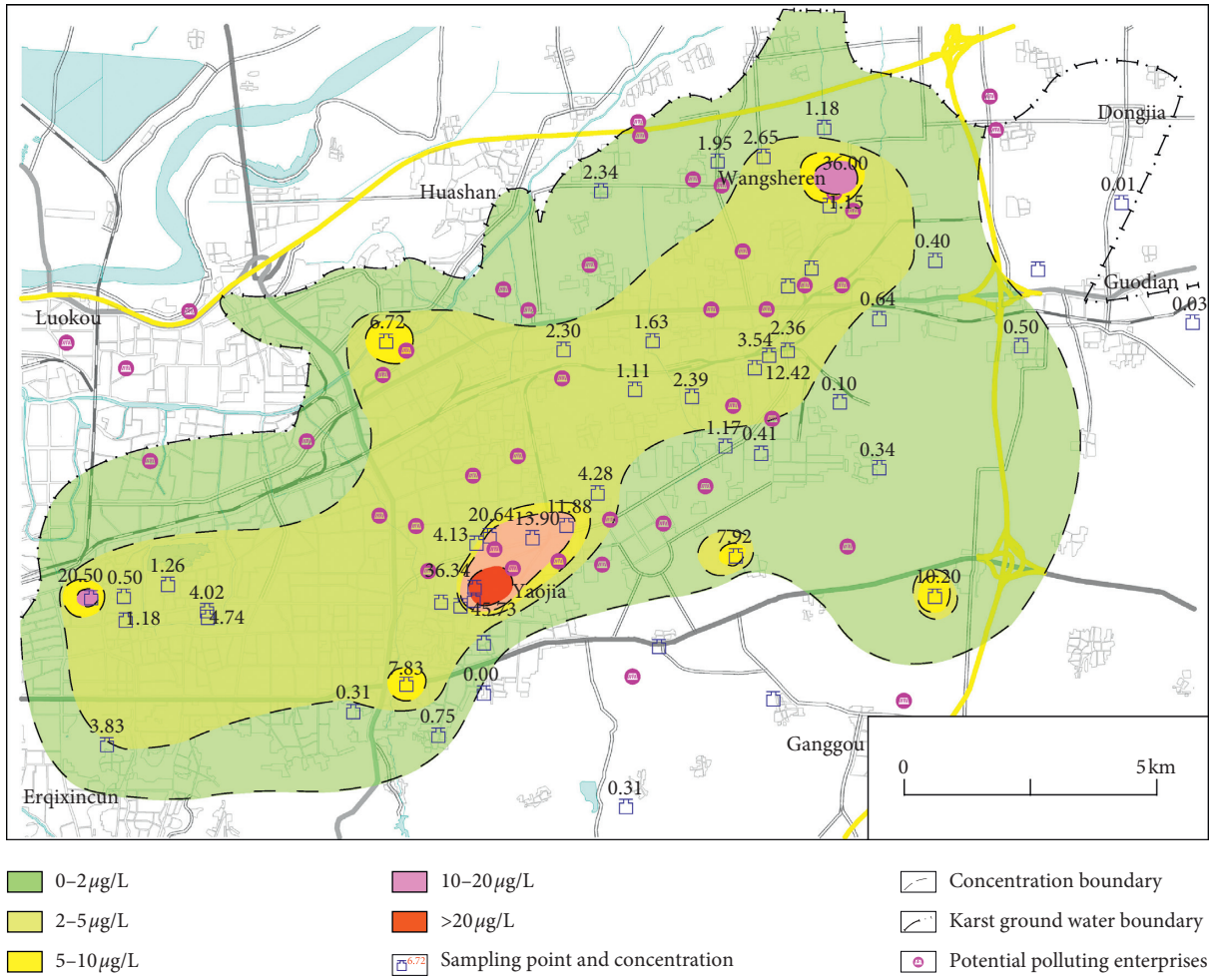

Figure 6: Distribution of total toxic organic compounds in fractured karst water in northeast spring area.

40.54%, followed by carbon tetrachloride and tetrachloroethylene, with a detection rate of 20.95% and trichloroethylene with a higher detection rate, with a detection rate of 16.89% (Figure 5).

The eastern outskirts of Jinan city are the key areas of organic pollution. There are many kinds of toxic organic compounds detected and the total amount is high, forming a relatively obvious pollution halo (Figure 6).

The spatial distribution of trichloromethane and carbon tetrachloride was analyzed. The karst water subsystem and the north part of Baiquan karst water subsystem in Jinan urban area are the main distribution areas of the two (Figures 7 and 8), which have obvious correlation with the intensive distribution of industrial enterprises in the northeast of the urban area.

3.2. Quality Evaluation and Classification

3.2.1. Toxic Heavy Metals. Quality evaluation was carried out according to the groundwater quality standard GB/T 14848-2017 in which groundwaters meet standards I, II, III, IV, and V. Groundwater which meets standards I and II is suitable for all kinds of uses, while groundwater which meets standard III is mainly applicable to centralized drinking water sources and industrial and agricultural water. Groundwater which meets standard IV is suitable for agriculture and some industrial water, and with proper treatment, the water can be used for drinking water, while groundwater which meets standard V is not suitable as a drinking water source and can only be selected to use according to certain other purposes. For 194 fissure karst water samples, the concentrations of each toxic metal in each sample are compared against the standards (Table 3), and then the comprehensive quality evaluation of heavy metal was carried out (Table 4). Among all the samples, the number of heavy metal comprehensive quality exceeding class III standard samples accounted for 3.09%, indicating that the heavy metal index have little influence on the comprehensive quality of fissure karst water. The main impact compounds exceeding class III criteria were Cr^{6+} (2.58%) and As (0.52%).

Samples that contain toxic heavy metals in class III, class IV, and class V are mainly distributed in the northern part of the karst water subsystem and Baiquan karst water

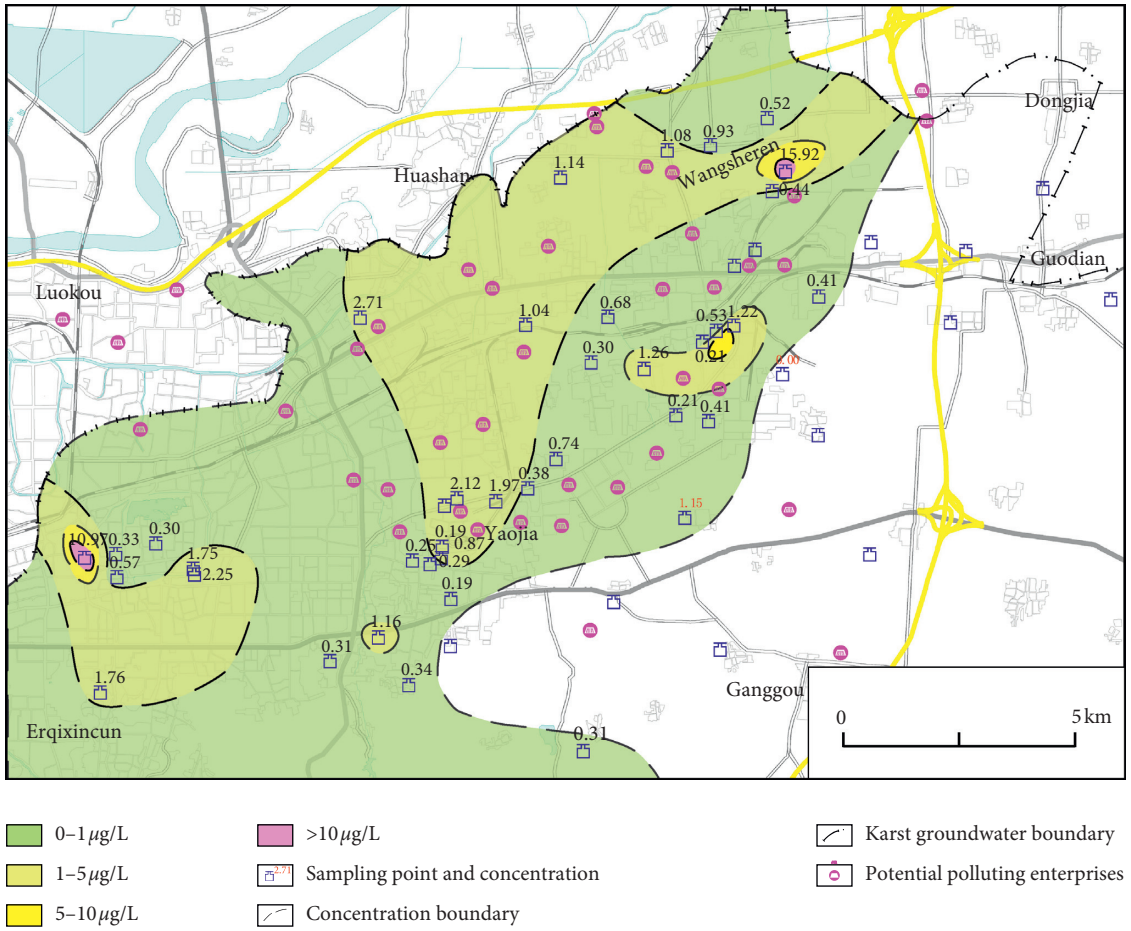

Figure 7: Distribution of the trichloromethane concentration in fractured karst water in northeast spring area.

subsystem in Jinan city, which are related to the production of industrial enterprises in this area, while the quality of the other areas is dominated by class I and class II (Figure 9).

3.2.2. Organic Compounds. Quality evaluation was carried out according to the groundwater quality standard GB/T 14848-2017. For 149 fissure karst water samples, the concentrations of each organic compound in each sample are compared against the standards (Table 5), and then the comprehensive quality evaluation was carried out (Table 6).

The quality evaluation of organic compounds shows that, among all samples, the number of classes IV and V standard samples was 14 samples, accounting for 9.40% of the total, indicating that toxic organic compounds have affected the comprehensive quality of fissure karst water in spring area.

In terms of spatial distribution (Figure 10), class I samples are widely distributed in the study area, while other class II and above samples are mainly distributed in the northern part of the karst water subsystem in Jinan urban area and the karst water subsystem in Baiquan, which is affected by human production and life. The main impact compounds exceeding class III standard were as follows: 12 samples of carbon tetrachloride (8.07%), including 11 samples of class IV water, 1 sample of class V water, and 2 samples of 1,1,2-trichloroethane (1.34%).

3.2.3. Influence of Toxic Substances on Comprehensive Quality Classification. In addition to the above toxic heavy metals and organic substances, 12 general chemical parameters, including pH, iron, manganese, zinc, aluminum, chloride ions, sulfate ions, total hardness, soluble total solids, total oxygen demand, ammonium ions, and sodium and 4 toxic inorganic parameters, including selenium, fluoride ions, nitrate ions, and nitrite, were selected for geochemical quality evaluation.

Quality evaluation was carried out according to the groundwater quality standard GB/T 14848-2017. For 149 fissure karst water samples, the concentrations of each general geochemical compound and each inorganic toxicology compound in each sample are compared against the standards (Tables 7 and 8), and then the comprehensive quality evaluation was carried out (Table 9, Figure 11).

Through comparative analysis, in the recharge area and runoff area of karst spring area, the groundwater impacted with toxic heavy metals are mainly classified as classes I or

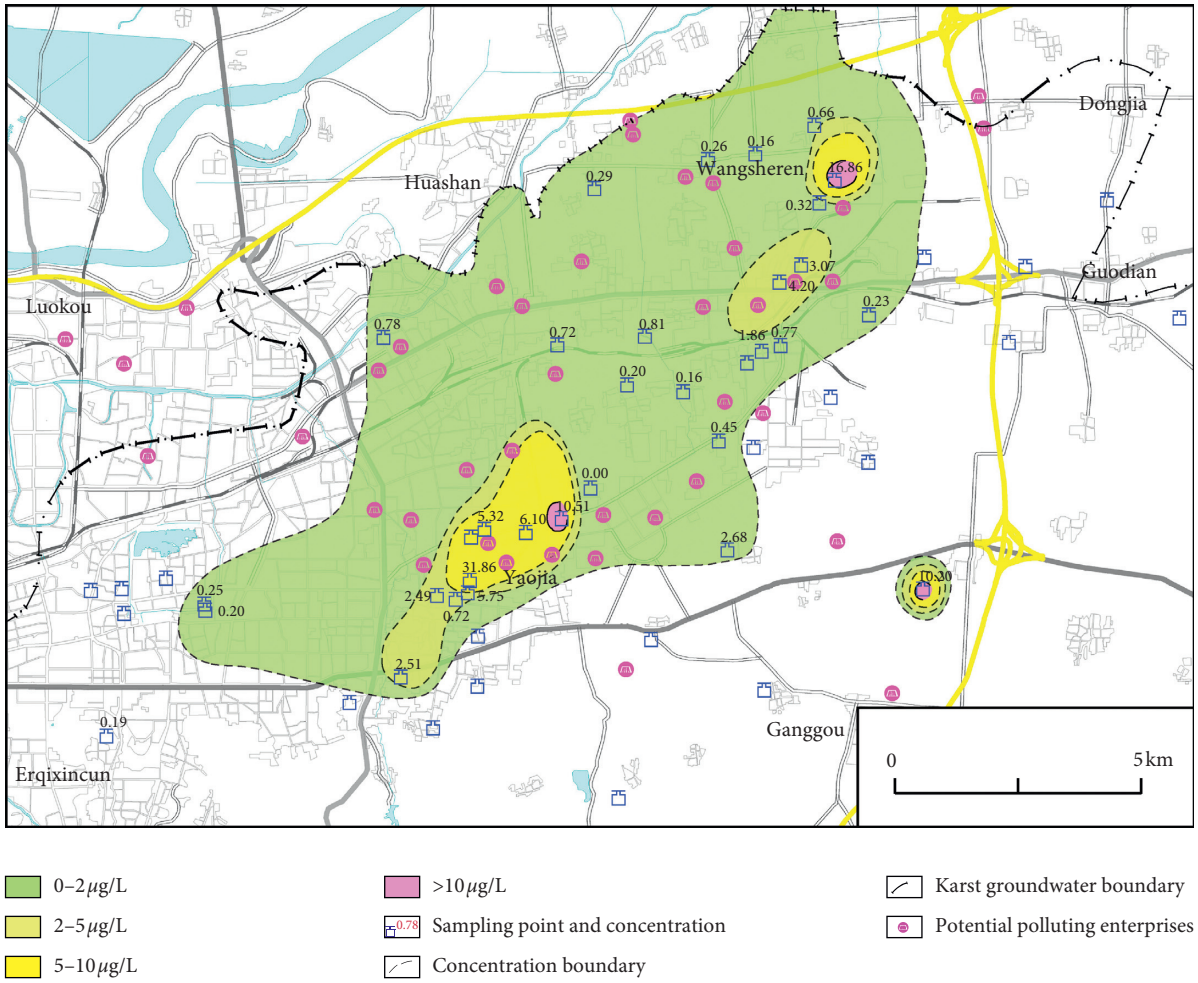

Figure 8: Distribution of the carbon tetrachloride concentration in fractured karst water in northeast spring area.

II and the groundwater impacted with toxic organic compounds are basically classified as class I, while groundwater impacted by the geochemical indicators are classified as classes III or IV, so the impact of the toxic heavy metals or toxic organic compounds is low compared with the impact of the geochemical indicators. In the drainage area of spring area, especially the southwest and northeast of Jinan urban area, the evaluation results of toxic heavy metals and toxic organic compounds are relatively consistent with the comprehensive quality evaluation results, which are classes IV or V, so the contribution rate is relatively high.

3.3. Source Analysis. Distribution of toxic substances has obvious correlation with historical and current industrial layout, and its concentration has persistence and inheritance. In terms of spatial distribution, according to incomplete statistics, there are 835 potential pollution enterprises in the current study area, mainly in the electromechanical, chemical, and steel smelting categories (Figure 12). Its distribution has obvious regional characteristics, mainly distributed in urban built-up areas, economic development zones, and near traffic trunk lines. Historically, the advantageous industries in Jinan urban areas include machinery, textile, steel, chemical light industry, food, and building materials. In recent years, machinery (high-performance, high-added value mechanical products, and metallurgical products), vehicles (advanced heavy vehicles, modified automobiles, and motorcycles), electricity (emerging industries electronic products and high-grade household appliances), chemical (modern biomedical chemical, fine chemical, and chemical fibers) have been developed and have become the city's four leading industries. The new enterprises may cause pollution to both soil and groundwater, which brings new challenges to contaminated soil remediation [25] and wastewater treatment [26]. Analyzing history and current situation, we concluded that the production activities of industrial enterprises should be the main reasons for the detection of toxic substances in karst water in Jinan. Toxic heavy metals may mainly originate from Jinan iron and steel plant, Jinan Huangtai power plant, and other smelting and thermal enterprises, while organic substances may mainly originate

Table 3: Quality evaluation of toxic heavy metals in fractured karst water.

Evaluating compounds	I		II		III		IV		V	
	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)
As	≤0.001	99.48	≤0.001	0	≤0.01	0	≤0.05	0.52	>0.05	0
Cd	≤0.0001	56.19	≤0.001	41.75	≤0.005	2.06	≤0.01	0	>0.01	0
Cr^{6+}	≤0.005	89.18	≤0.01	4.64	≤0.05	3.61	≤0.10	1.55	>0.10	1.03
Pb	≤0.005	99.48	≤0.005	0	≤0.01	0.52	≤0.10	0	>0.10	0
Hg	≤0.0001	100	≤0.0001	0	≤0.001	0	≤0.002	0	>0.002	0

Table 4: Comprehensive quality evaluation of toxic heavy metals in fractured karst water.

Quality classification of toxic heavy metals in karst water	Number of samples	Percentage (%)
I	99	51.03
II	77	39.69
III	12	6.19
IV	4	2.06
V	2	1.03
Total	194	100

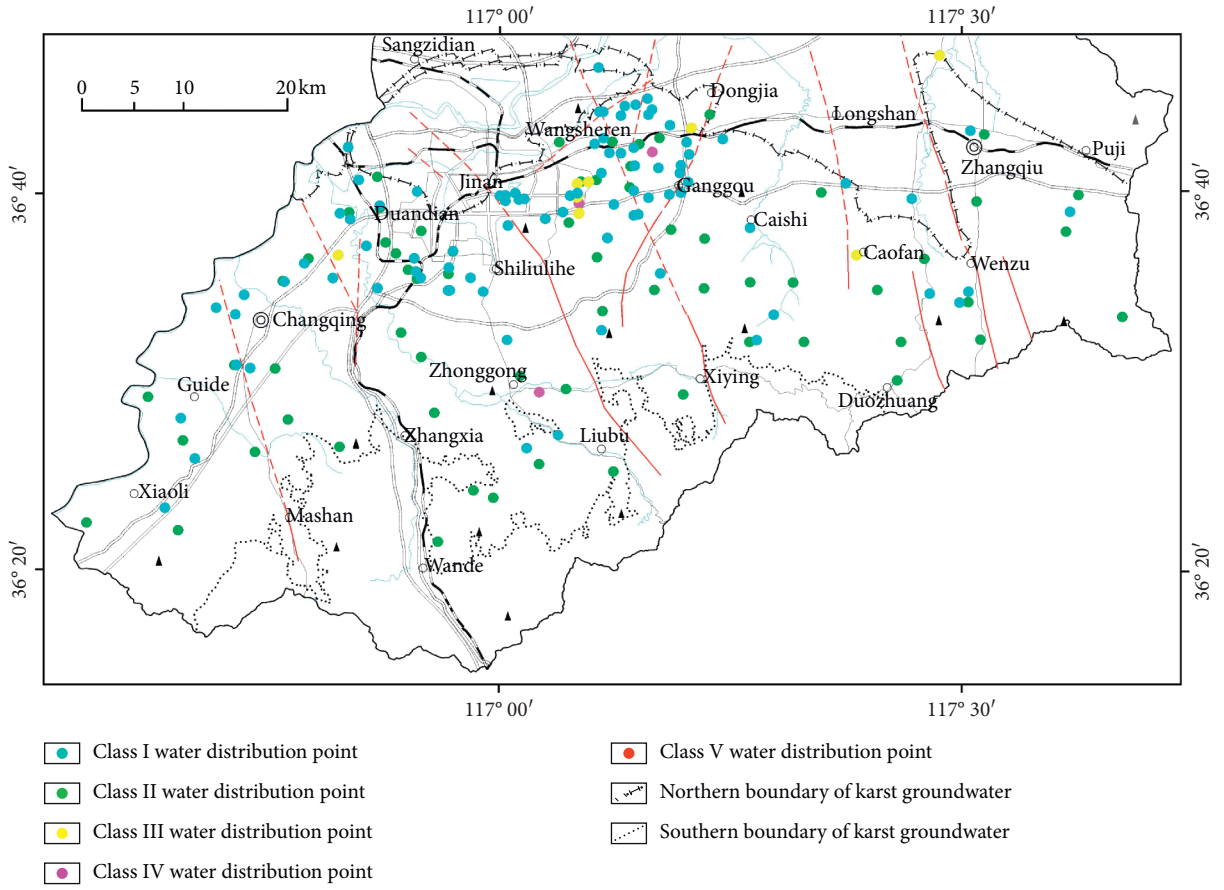

Figure 9: Comprehensive quality evaluation of toxic heavy metals in fractured karst water.

from Jinan refinery, Qilu pharmaceutical enterprise, Jinan yuxing chemical plant, and other chemical and pharmaceutical enterprises.

The long-term persistence of toxic substance concentration in the study area is further illustrated by the test results in the 1980s. In terms of toxic heavy metals, 212 fractured karst water samples were collected in Jinan urban area and eastern and western suburbs for two consecutive years in the early 1980s. The detection rates of hexavalent chromium, mercury, and arsenic were 41.51%, 8.02%, and 1.89%, respectively. Hexavalent chromium samples were mainly distributed in three regions, two of which were located in the northeast of Jinan urban area, with Wangsheren town and Qilihe, Huangtai as the distribution centers, Jinan iron and steel plant and Huangtai power plant, and Jinan second iron and steel plant as the main pollution sources; the other was located in the southwest of Jinan city, Baima mountain to Duandian area. The above areas are also the main distribution areas of current industrial enterprises. The distribution of toxic heavy metal elements in the 1980s is consistent with this result, which indicates that heavy metals mainly originate from industrial production and have a long-term nature. On the one hand, groundwater pollution itself is not easy to eliminate; on the other hand, it is also related to the long-term existence of enterprise production activities.

In terms of toxic organic compounds, the detection rate of volatile phenol was 4.25% in the 1980s, and its

Table 5: Quality evaluation of organic compounds in fractured karst water.

Evaluating compounds	I		II		III		IV		V	
	Groundwater quality standard (μg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (μg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (μg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (μg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (μg/L)	Fraction of samples meeting the standard (%)
Trichloromethane	≤0.5	77.85	≤6	20.13	≤60	2.01	≤300	0	>300	0
Carbon tetrachloride	≤0.5	87.25	≤0.5	0	≤2.0	4.70	≤50.0	7.38	>50.0	0.67
1,1,1-Trichloroethane	≤0.5	100	≤400	0	≤2000	0	≤4000	0	>4000	0
Trichloroethylene	≤0.5	91.95	≤7.0	7.38	≤70.0	0.67	≤210	0	>210	0
Tetrachloroethylene	≤0.5	92.62	≤4.0	7.38	≤40.0	0	≤300	0	>300	0
Dichloromethane	≤1	100	≤2.0	0	≤20.0	0	≤500	0	>500	0
1,2-Dichloroethane	≤0.5	100	≤3.0	0	≤30.0	0	≤40.0	0	>40.0	0
1,1,2-Trichloroethane	≤0.5	98.66	≤0.5	0	≤5.0	0	≤60.0	0	>60.0	1.34
1,2-Dichloropropane	≤0.5	98.66	≤0.5	0	≤5.0	1.34	≤60.0	0	>60.0	0
Bromoform	≤0.5	95.97	≤10.0	4.03	≤100	0	≤800	0	>800	0
Vinyl chloride	≤0.5	100	≤0.5	0	≤5.0	0	≤90.0	0	>90.0	0
1,1-Dichloroethylene	≤0.5	100	≤3.0	0	≤30.0	0	≤60.0	0	>60.0	0
cis-1,2-Dichloroethylene	≤0.5	95.3	≤5.0	3.36	≤50.0	1.34	≤60.0	0	>60.0	0
Chlorobenzene	≤0.5	100	≤60.0	0	≤300	0	≤600	0	>600	0
Phthalates	≤0.5	100	≤200	0	≤1000	0	≤2000	0	>2000	0
Dichlorobenzene	≤0.5	100	≤30.0	0	≤300	0	≤600	0	>600	0
Benzene	≤0.5	100	≤1.0	0	≤10.0	0	≤120	0	>120	0
Toluene	≤0.5	100	≤140	0	≤700	0	≤1400	0	>1400	0
Ethylbenzene	≤0.5	100	≤30.0	0	≤300	0	≤600	0	>600	0
Ditoluene	≤0.5	100	≤100	0	≤500	0	≤1000	0	>1000	0
Styrene	≤0.5	100	≤2.0	0	≤20.0	0	≤40.0	0	>40.0	0
Total BHC	≤0.01	95.97	≤0.50	4.03	≤5.00	0	≤300	0	>300	0
γ-BHC (lindane)	≤0.01	100	≤0.20	0	≤2.00	0	≤150	0	>150	0
Total DDT	≤0.01	100	≤0.10	0	≤1.00	0	≤2.00	0	>2.00	0
Hexachlorobenzene	≤0.01	100	≤0.10	0	≤1.00	0	≤2.00	0	>2.00	0
Benzo(a) pyrene	≤0.002	100	≤0.002	0	≤0.01	0	≤0.50	0	>0.50	0

Table 6: Comprehensive quality evaluation of organic compounds of fractured karst water.

Quality classification of organic index of fractured karst water	Number of samples	Percentage
I	105	70.47
II	21	14.09
III	9	6.04
IV	11	7.38
V	3	2.02
Total	149	100

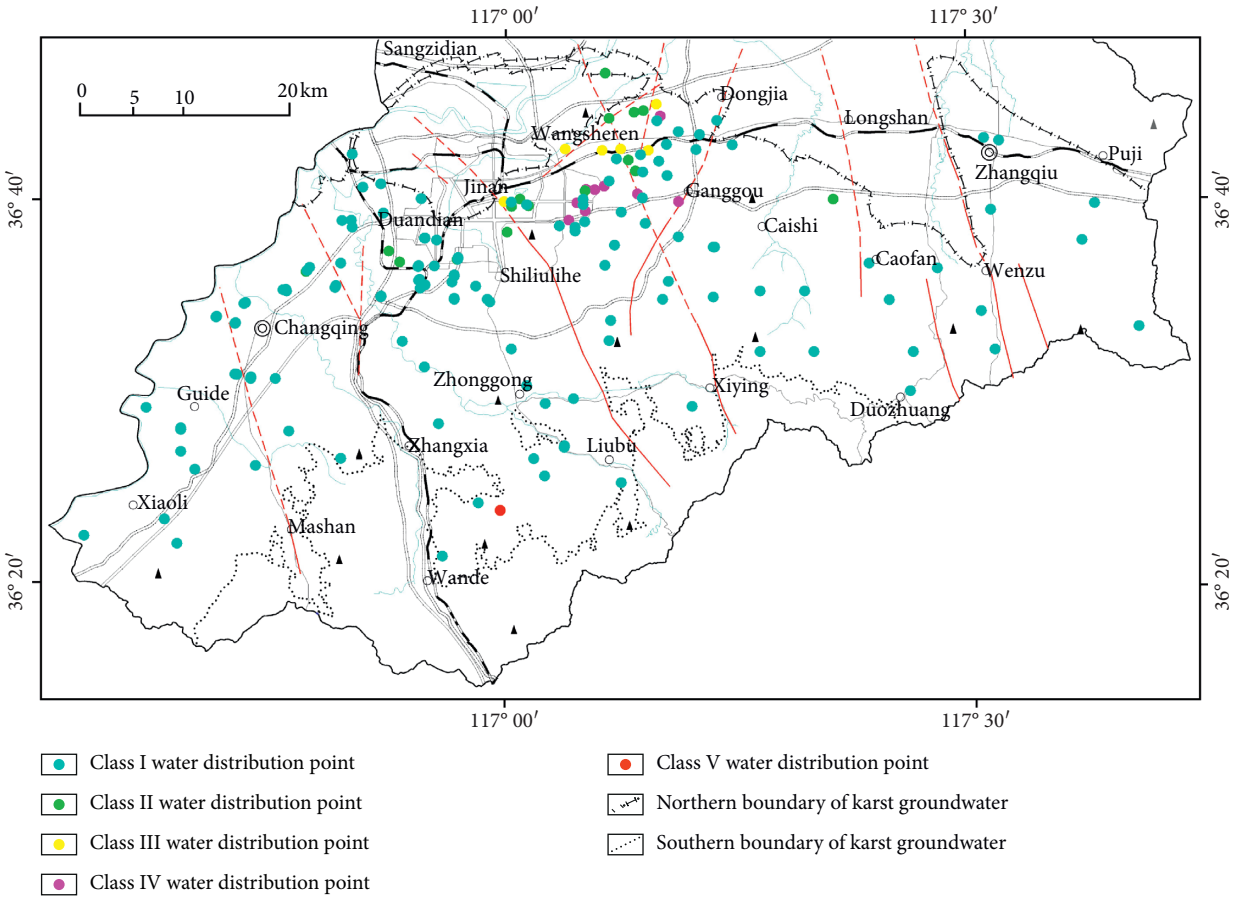

Figure 10: Quality evaluation of organic compounds of fractured karst water.

samples were mainly located near Licheng pesticide factory and Jinan light industry chemical factory at that time. Fifteen samples of fractured karst water were collected to test HCH and DDT in organochlorine pesticides. The detection rates of HCH and DDT were 100% and 93%, respectively, showing a general distribution. Organochlorine pesticides have been discontinued in Jinan for nearly 30 years. Organochlorine pesticides were still detected in 10 of 148 samples collected this time, indicating the persistence of karst water pollution.

The source of trichloromethane and carbon tetrachloride with the highest detection rate of toxic organic compounds was analyzed. Trichloromethane is an important raw material for organic synthesis, which is used to make lipids, rubber, paints, synthetic fibers, plastics, etc. Enterprises producing methane-based chlorinated hydrocarbons are a frequent source of pollution for trichloromethane entering the environment. Carbon tetrachloride is mainly used in the production of chlorofluorocarbon (CFC) refrigerants, foaming agents, and solvents, as well as in the manufacture of paints and plastics, as well as in metal cleaning, fumigants, and other solvents. Accidents in the above industries may cause the contamination of karst water by both substances. The detected water samples of trichloromethane and carbon tetrachloride are mainly distributed in the eastern part of the urban area, which has obvious correlation with the industrial

Table 7: Quality evaluation of general geochemical compounds in fractured karst water.

Evaluating compounds	I		II		III		IV		V	
	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)
pH	pH 6.5 to 8.5	100	pH 6.5 to 8.5	0	pH 6.5 to 8.5	0	pH 5.5 to 6.5 or 8.5 to 9.0	0	pH <5.5 or >9.0	0
Fe	≤0.1	81.21	≤0.2	8.05	≤0.3	3.36	≤2.0	6.71	>2.0	0.67
Mn	≤0.05	97.99	≤0.05	0	≤0.10	2.01	≤1.50	0	>1.50	0
Zn	≤0.05	91.28	≤0.5	8.05	≤1.00	0	≤5.00	0.67	>5.00	0
Al	≤0.01	63.09	≤0.05	20.81	≤0.20	14.77	≤0.50	0.67	>0.5	0.67
Cl^-	≤50	69.8	≤150	28.86	≤250	1.34	≤350	0	>350	0
SO_4^{2-}	≤50	15.44	≤150	69.8	≤250	11.41	≤350	3.36	>350	0
Total hardness	≤150	0	≤300	19.46	≤450	57.72	≤650	22.15	>650	0.67
TDS	≤300	12.08	≤500	56.38	≤1000	30.87	≤2000	0.67	>2000	0
DO	≤1.0	97.32	≤2.0	1.34	≤3.0	1.34	≤10.0	0	>10.0	0
NH_4^+ (In N)	≤0.02	99.33	≤0.10	0	≤0.50	0.67	≤1.50	0	>1.50	0
Na^+	≤100	100	≤150	0	≤200	0	≤400	0	>400	0

Table 8: Quality evaluation of inorganic toxicology compounds in fractured karst water.

Evaluating compounds	I		II		III		IV		V	
	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)	Groundwater quality standard (mg/L)	Fraction of samples meeting the standard (%)
Se	≤0.01	100	≤0.01	0	≤0.01	0	≤0.1	0	>0.1	0
F^-	≤1.0	20.81	≤1.0	51.68	≤1.0	26.17	≤2.0	0.67	>2.0	0.67
NO_3^- (In N)	≤2.0	3.36	≤5.0	16.11	≤20.0	67.79	≤30.0	8.05	>30.0	4.7
NO_2^- (In N)	≤0.01	90.6	≤0.1	5.37	≤1.00	2.01	≤4.8	1.34	>4.8	0.67

Table 9: Comprehensive quality evaluation of fractured karst water.

Comprehensive quality classification of fractured karst water	Number of samples	Percentage (%)	Distribution area (km^2)	Percentage (%)
II	12	8.05	152.49	5.56
III	82	55.03	2414.32	88.04
IV	40	26.85	151.75	5.54
V	15	10.07	23.72	0.86
Total	149	100	2742.28	100

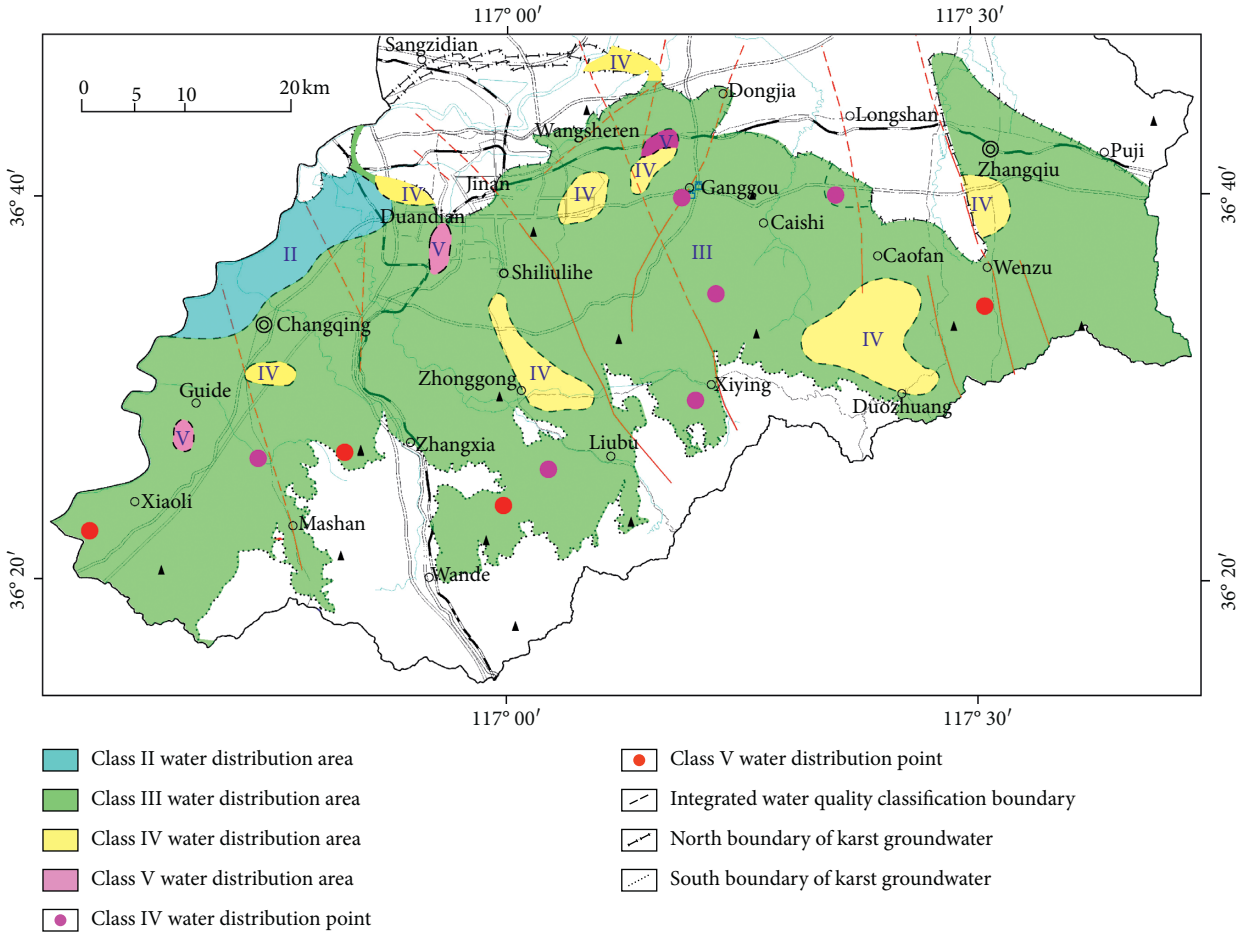

Figure 11: Comprehensive quality distribution of fractured karst water.

enterprises such as petrochemical, paint, plastics, and steel which have been gathered for a long time in the eastern part of the urban area.

Carbon tetrachloride was taken as an example to analyze the persistence of toxic substance concentration. Because of the barrier of gabbro in the north of the spring area in Jinan area, it is difficult for surface carbon tetrachloride to enter the karst water directly by leaching, and at the same time, carbon tetrachloride is rarely used by enterprises nowadays, which can basically exclude the possibility that the existing pollution sources cause carbon tetrachloride exceeding the standard in karst water. In the previous studies, carbon tetrachloride in Xuzhou, China, can cause continuous pollution of groundwater for more than 12 years [13], and it takes a long time to eliminate the impact of carbon tetrachloride on water quality. According to investigation, Jinan chemical plant has been using carbon tetrachloride to produce freon refrigerant from 1974 to 1996, with annual consumption of up to 5000 tons; among them, the plant directly produced carbon tetrachloride from 1989 to 1992, with annual production of up to 500 tons. In addition, companies such as Bluestar petroleum have used or produced carbon tetrachloride in small quantities. Therefore, it is considered that the serious pollution of carbon tetrachloride in fissure karst water in northeastern Jinan is caused by the emission or leakage of carbon tetrachloride produced or used in the history of the above enterprises.

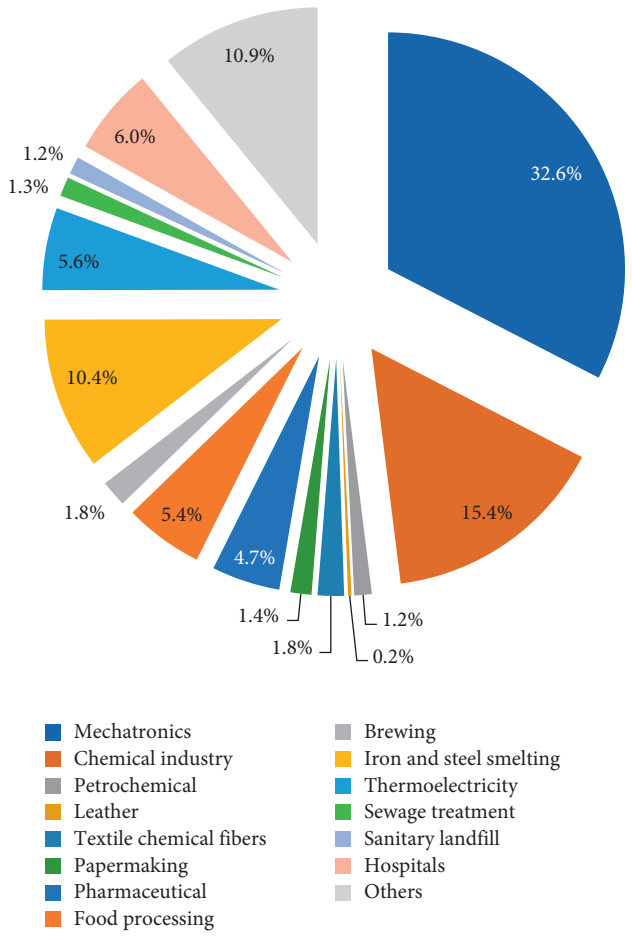

Figure 12: Classification of potential pollution enterprises in Jinan area.

4. Conclusion

The comprehensive evaluation of groundwater in a karst aquifer system that provide groundwater to an industrial area with more than six million people is of great significance for understanding the main toxic substances and the water quality. The study provides scientific understanding which is beneficial to the improvements of groundwater quality and the sustainable development of Jinan's economy, society, and ecology. The toxic substances of karst water in Jinan are mainly distributed in the northern part of the Jinan karst water subsystem and the Baiquan karst water subsystem, while in other areas, the toxic substances have comparatively low detection rates and low concentrations. The distribution of karst water quality is determined by the concentration of evaluation indexes, and the northeast and southwest parts of Jinan urban area are the main distribution areas exceeding class III standard. In the recharge area and the runoff area of the karst spring area, the influence of toxic substances on the comprehensive quality classification is relatively low, and in the drainage area, the influence is relatively high. Compared with toxic heavy metals, organic compounds contribute more to the comprehensive quality of karst water.

Toxic substances have been widely distributed in Jinan karst water. Among the toxic heavy metals, the detection rates of cadmium, lead, hexavalent chromium, arsenic, and mercury were in order from high to low. The detection rates of organic compounds from high to low are trichloromethane, carbon tetrachloride, tetrachloroethylene, trichloroethylene, etc. The above compounds are important compounds to control the comprehensive quality of karst groundwater.

The distribution of toxic substances has an obvious correlation with the historical and current industrial layout, and its concentration has persistence and inheritance. The production activities of industrial enterprises are the main reasons for the detection of toxic substances in karst water in Jinan. On the one hand, the long-term persistence of toxic substances is related to its own difficulty to eliminate, that is, once they enter the groundwater, it is difficult to degrade or lose; on the other hand, it is also related to the long-term nature of the production activities of enterprises, that is, there may be persistent toxic substances entering the groundwater.

Effective measures should be taken to improve the quality of karst groundwater in Jinan to serve the needs of environmental restoration and ecological civilization construction. One is to strengthen the supervision and improve the process to minimize the leakage of new toxic substances; the other is to treat and repair existing pollution by appropriate engineering and technical means; the third is to strengthen the monitoring to provide data support for scientific evaluation of the evolution of karst water quality, government consultation, and decision-making and the implementation of rehabilitation projects.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Disclosure

Hao Shang and Xiaofan Qi are co-first authors.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Hao Shang and Xiaofan Qi have contributed equally to this work.

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