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Source Apportionment and Health Risk Assessment of Groundwater Potentially Toxic Elements (PTEs) Pollution Characteristics in an Accident Site in Zhangqiu, China

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Abstract: In order to understand the pollution degree and source of potentially toxic elements (PTEs) in groundwater around the accident site and evaluate their harm to human health, 22 groundwater samples were collected around the accident well, and the contents of As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, CH_2Cl_2 and $C_2H_4Cl_2$ were determined. On the basis of water quality evaluation, the source apportionment method combining qualitative and quantitative analysis was used to determine the main sources of PTEs in the region, and the health risk assessment model was used to evaluate the health risk of PTEs to the human body. The results show that pH, TDS, Th and COD all exceed the standard to varying degrees, among which TH is the index with the largest number exceeding the standard. The quality of the groundwater environment in the study area is at a very poor level, and the F value is between 7.25 and 8.49. The exposure results model showed that there was no non-carcinogenic risk of PTEs in the study area, and the health risk of oral intake in the exposed population was greater than that of skin contact. Compared with adults, children were more vulnerable to the health risk stress of PTEs in groundwater. The total carcinogenic risk is higher than the total non-carcinogenic risk. As, Cd and Cr are the primary factors causing carcinogenic health risks in this area. Principal component analysis (PCA) was used to analyze the sources of PTEs in groundwater, and three principal components were extracted. It was preliminarily determined that PTE pollution was mainly related to agricultural sources, anthropogenic industrial sources and industrial sedimentation sources. The results of positive definite factor matrix analysis (PMF) were basically similar to those of PCA, but PMF further clarified the contribution rate of three pollution sources, among which agricultural sources contributed the most to the accumulation of PTEs.

Keywords: health risk assessment; groundwater; PTEs; PMF; source analysis

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1. Introduction

Groundwater is a kind of extensive and fragile natural resource that is very important for human survival and development. According to statistics, the total amount of water resources in China in 2022 was 2708.81 billion m^3, of which 792.44 billion m^3 was underground water resources, accounting for about 30% of the total water resources [1]. Groundwater resource storage and water security play an important role in regional economic development and residents' lives. Especially in northern China, most of the water used in human daily life comes from groundwater [2].

However, in recent years, with the rapid growth of the economy and population, urbanization and industrialization have rapidly improved. At the same time, due to the large discharge of industrial waste, agricultural waste and municipal solid waste, the quality of the groundwater environment has been seriously threatened [3–7], especially groundwater pollution with potentially toxic element (PTE) pollution as an important source of pollution. According to the 2006 report of the World Health Organization, nearly 80% of human diseases worldwide are caused by groundwater pollution. Heavy metal pollution and organic pollution in groundwater are some of the causes of biological and ecosystem toxicity [8].

These typical PTEs have strong neurotoxicity, long-distance migration and difficult degradation [9–11]. PTEs bioaccumulate in the process of transferring along the food chain, which has a more serious impact on the ecological environment and human health [12–15]. For example, large amounts of toxic elemental mercury have been found in fish or other animals in remote Arctic regions [16]. In recent years, scholars at home and abroad have focused on different areas and different types of soil around coal-fired power plants. Among the many evaluation methods, the Nemerow pollution index method, principal component analysis method, gray system method and fuzzy comprehensive evaluation method, which add the uncertainty theory of pollution to the research method, are the most frequently used. The health risk model was used to carry out research on the human health risk assessment of PTEs [17–20]. There are also some studies on the qualitative source identification and quantitative source analysis of pollutant source analysis methods such as joint correlation analysis, cluster analysis and the positive matrix factorization model [21–23]. However, there are few reports on the quantitative source apportionment of PTEs in groundwater, especially the combination of the dual quantitative source apportionment receptor model for source apportionment and mutual comparison.

Due to the existence of factories around the study area, there are unknown people dumping waste liquid in the accident well, resulting in environmental pollution incidents. Therefore, this paper selects 22 groundwater sampling points at an accident site in Zhangqiu City, Shandong Province, China. According to the detection results of various indicators of groundwater in this area, based on the analysis and determination of PTE content in groundwater, the single-factor pollution index and Nemerow comprehensive pollution index method were used to comprehensively evaluate the PTE pollution characteristics of groundwater. Based on the IBM SPSS Statistics 26.0 model of correlation analysis combined with principal component analysis and the positive matrix factorization model, the PTE pollution source of groundwater was quantitatively explained, and the health risk system proposed by USEPA was used to evaluate the health risk of PTEs in groundwater to the human body in two ways. It provides a scientific basis for maintaining the safety of the groundwater environment and human health.

2. Materials and Methods

2.1. Study Area

Zhangqiu District is located in the eastern region of Jinan City, with an area of 1719 km^2. It is connected to the Zhoucun District of Zibo City in the east and the Daiyue District of Tai an City in the south. The traffic in the area is convenient. Zhangqiu District is located on the northern foot of Taiyi Mountain, bordering on the North China Plain [24]. The Great Wall Ridge stretches to the south, and Changbai Mountain stands to the east. The terrain is tilted from southeast to northwest and from south to north, followed by mountains, hills, plains and depressions. It is a continental climate in the warm temperate monsoon region. The four seasons are distinct, and the rain and heat occur in the same season. Spring is dry and windy, summer rainfall is concentrated, autumn is mild and cool and winter snow is less dry and cold [25]. The accident site is located in the surrounding area of Shanggao Village Coal Mine in Zhangqiu City, Shandong Province.

The southern part of the Tuozhangqiu belongs to the Luxi uplift, and the northern part belongs to the Jiyang sag. The geological structure is dominated by monoclinic strata, with a strike of 60° NW and a dip angle of 7° to 13°. The strata exposed in the study area are mainly Quaternary and Ordovician, and the remaining strata are less or not exposed [26]. The sedimentary sequence of each geological age is the Archean metamorphic rock series, the Paleozoic sedimentary rock series, the Mesozoic sedimentary rock series and the Cenozoic sedimentary rock series [27]. The larger synclines in the study area include the Wenzu–Bucun syncline and the Xilanggou syncline. The faults and fissures are mostly NNW and NNE, and the larger faults are the Wenzu fault, Yuwangshan fault, Ganquan fault, Songjiazhuang fault and so on.

The hydrogeological unit of the study area belongs to the upstream runoff area of the Mingshui spring basin. The piedmont zone in the northern part of the study area is mainly loose rock pore water. The main aquifer of carbonate rock fissure karst water is the Wuyangshan Formation, which is mainly located in the south and exposed to the surface. The karst fissure water of clastic rock and carbonate rock is mainly coal-bearing strata. The bedrock weathering fissure water is mainly distributed in the northern part of the study area. Artificial mining discharge is an important discharge form of karst water in the area. Because the area is mainly a monoclinic structure, confined groundwater is often formed in the continuous distribution section of sandstone.

2.2. Sampling and Analysis

Combined with the geological structure, environment and human activities, according to 'the technical guidelines for the sampling of volatile organic compounds in soil and groundwater' (HJ 1019-2019), 'Groundwater environment investigation and evaluation work guide', 'Groundwater environment monitoring technical specification' (HJ 164-2020), the point layout is required, 22 monitoring wells are set up and a total of 22 groups of groundwater samples are collected. The groundwater sampling points are shown in Figure 1. Taking the accident well as the center, 22 monitoring wells were taken around the accident well. Clean, dry polyethylene plastic bottles were used to take water samples, and the sample pretreatment was completed within 24 h.

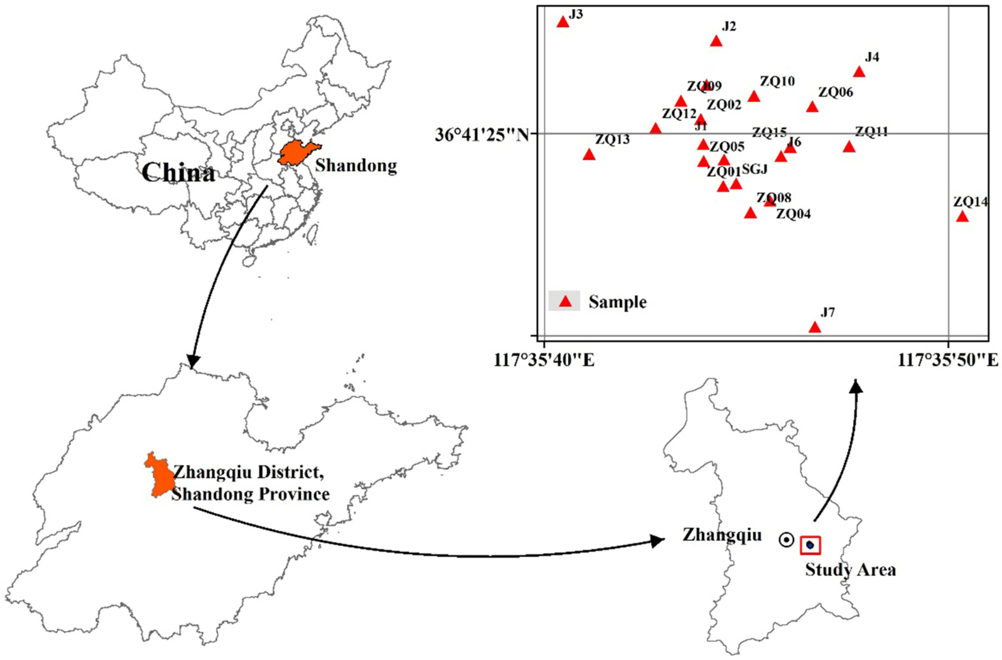


Figure 1. The schematic diagram of sampling points in the study area.

Inductively coupled plasma mass spectrometry (ICP-MS) (ICP-MS, Thermo X Series 2, Waltham, MA, USA) is used to detect heavy metal ions in groundwater samples. Volatile organic compounds in water samples are detected according to 'Determination of volatile organic compounds in water quality-Purge and trap/gas chromatography-mass spectrometry' (HJ 639-2012). Quality assurance and control are carried out by means of method blank and matrix addition. We use a purge and trap device (ATOMX-XYZ 1090L0429, Mason, OH, USA), and the chromatographic mass spectrometer is Agilent 8890-5977B (Agilent, Santa Clara, CA, USA) [28]. All tests are performed in triplicate to ensure the accuracy of the analysis. The error of parameter analysis is detected by the cation–anion concentration balance method, and the measurement error is less than 5%.

2.3. Groundwater Quality Assessment

The comprehensive evaluation method of groundwater quality is the evaluation method recommended by the 'Groundwater Quality Standard' (GB/T 14848-2017) [29]. The specific steps are as follows: Firstly, the element indexes were determined according to 'Groundwater Quality Standard' [29], and the pollution indexes of single component and multiple components were calculated with the limitation of class III water quality standard as the evaluation standard. Then, the pollution grade of sampling points was determined by combining the classification standards of multiple indexes [30,31].

2.3.1. Single-Factor Evaluation Method

The measured concentration value is compared with the limit value in the evaluation standard to determine the pollution level of the pollutant. The formula is as follows:

$$\mathrm{P_{ki}} = \frac{\mathrm{c_{ki}}}{\mathrm{S_{ij}}} \tag{1}$$

In the formula, $\mathrm{P_{ki}}$ is the pollution index of the pollution index i in the water quality sample of the k monitoring well; $\mathrm{c_{ki}}$ is the measured concentration of the pollution index i in the water quality sample of the k monitoring well; $\mathrm{s_{ij}}$ is the limit value of pollution index i in GB/T 14848-2017 j water quality standard.

The pollution level is divided into six grades, and the degree of pollution has never reached serious pollution. The specific evaluation and grading standards of single-factor evaluation are shown in Table 1.

Table 1. Single-factor pollution score levels.

Pki	Class of Pollution	Pollution Level
≤0	I	uncontaminated
0~1	II	light pollution
1~3	III	moderate pollution
3~6	IV	more serious pollution.
6~10	V	heavy pollution
>10	VI	extremely heavy pollution

2.3.2. Nemerow Comprehensive Evaluation Method

The comprehensive evaluation method of the Nemerow index is used to obtain the environmental pollution index by comparing the measured value of the water quality monitoring index with the environmental standard value and then calculating the weight on the basis of the obtained environmental pollution index, which can accurately take into account the influence of the maximum value and avoid the influence of personal subjective factors in the process of weighted calculation. The formula is as follows:

$$F_i = \frac{c_{ki}}{S_{ij}} \tag{2}$$

$$\overline{F} = \frac{1}{n}\sum_{i=1}^{n} F_i \tag{3}$$

$$F = \sqrt{\frac{F_{max}^2 + \overline{F}^2}{2}} \tag{4}$$

In the formula, c_{ki} is the measured concentration of the pollution index i in the water quality sample of the k monitoring well; s_{ij} is the limit value of pollution index i in GB/T 14848-2017 j water quality standards; F_{max} is the maximum value of each pollution index F_i, which is dimensionless; $\overline{F}$ is the average value of each pollution index F_i, which is dimensionless. The classification of the Nemerow comprehensive pollution index is shown in Table 2. The pollution level is divided into five grades, and the pollution degree is superior to the range.

Table 2. Nemerow comprehensive evaluation score levels.

F	Class of Pollution	Pollution Level
≤0.8	I	superior
0.8~2.5	II	better
2.5~425	III	good
4.25~7.2	IV	worse
>7.2	V	range

2.4. Health Risk Assessment Model

PTEs in groundwater mainly harm human health through oral intake (including direct drinking water and indirect drinking water) and skin contact (including bathing and swimming). These two methods account for more than 90% of the pollutants ingested in or in contact with the human body. PTEs in groundwater in the study area can be divided into chemical carcinogenic elements (As, Cd, Cr, CH_2Cl_2 and $C_2H_4Cl_2$) and chemical non-carcinogenic elements (Cu, Zn, Ni, Hg and Pb). Their risk characterization is mainly carried out in two aspects, namely non-carcinogenic risk assessment and carcinogenic risk assessment [32].

Recipients exposed to groundwater in and around industrial areas can be divided into adults and children. The US Environmental Protection Agency (USEPA) has developed a human health risk assessment model. Based on this model, different calculation methods are used to calculate the health risks caused by oral intake and skin contact [32]. The groundwater health risks in China are mostly based on foreign models and parameters. The actual evaluation results will be affected by uncertainties such as system models, scenarios and human activities. Therefore, the exposure parameters of Shandong Province are used as much as possible in the specific calculation process to make the research results more in line with the actual situation of local people.

(1) Risk exposure through oral intake route: ADD_i, mg $(kg \times d)^{-1}$

$$ADD_i = \frac{c_w \cdot IR \cdot ED \cdot EF}{BW \cdot AT} \tag{5}$$

In the formula, c_w is the pollutant concentration, mg × L^{-1}; IR is drinking water intake, L × d^{-1}; EF is drinking water exposure frequency, d × a^{-1}; ED is the exposure period of drinking water, a; BW is the average body weight of the population in Shandong Province (the two groups are divided into adults and children), kg; AT is exposure time (non-carcinogenic exposure time and carcinogenic exposure time), d. Reference values of model parameters are in Table 3.

(2) Risk exposure of skin contact pathway, ADD_d, mg $(kg \times d)^{-1}$

$$ADD_d = \frac{c_w \cdot SA \cdot PC \cdot ET \cdot ED \cdot EF \cdot CF}{BW \cdot AT} \tag{6}$$

In the formula, c_w is the pollutant concentration, mg × L^{-1}; SA is the skin contact surface area, cm^2; PC is skin permeation constant, cm × h^{-1}; ET is the exposure time, h × d^{-1}; *EF* is the frequency of skin contact exposure, d × a^{-1}; *ED* is the duration of skin contact exposure, a; *CF* is the volume conversion factor, L × cm^{-3}. The reference values and units of model parameters are shown in Table 3.

(3) Risk characterization

The PTEs detected in the samples were divided into two categories, non-carcinogenic substances and carcinogenic substances, and their health risks are calculated according to Equations (7) and (8), respectively [33]. The values of RfD_i and SF_i are shown in Table 4.

$$R_i^n = \frac{ADD_i}{RfD_i} \times 10^{-6} \tag{7}$$

$$R_i^c = SF_i \times LADD_i \tag{8}$$

In the formula, R_i^c is the lifetime excess carcinogenic risk of carcinogenic pollutant *i* to the population for 70 years, which is dimensionless, $LADD_i$ is the daily average exposure dose of threshold chemical pollutants, mg (kg × d)$^{-1}$, and the calculation method is the same as *ADD*.

Table 3. Exposure measurement calculation parameters.

Exposure Pathways	Parameter	Unit	Adults	Children	Reference
oral ingestion	IR	L × d^{-1}	2.54	0.92	[33,34]
	EF	D × a^{-1}	365	365	[35]
	ED	a	30	6	[35,36]
	BW	kg	62.8	22	[33,34]
skin exposure	SA	cm^2	1.7 × 10^4	8100	[33,34]
	EF	D × a^{-1}	200	200	[35,37]
	ET	H × d^{-1}	0.173	0.145	[33,34]
	CF	L × cm^{-3}	0.001	0.001	[38]
	AT (non-carcinogenic)	d	ED × 365	ED × 365	[35]
	AT (carcinogenic)	d	74.68 × 365	10 × 365	[35]

Table 4. Skin permeation constant and reference dose of PTEs for oral and transdermal delivery [34–38].

PTEs	PC cm × h^{-1}	SF/mg × (kg × d)$^{-1}$		RFD/mg × (kg × d)$^{-1}$	
		Oral Ingestion	Skin Exposure	Oral Ingestion	Skin Exposure
As	1.8 × 10^{-3}	1.5	1.5	3.0 × 10^{-4}	3.0 × 10^{-4}
Cr	2.0 × 10^{-3}	0.501	20.0	3.0 × 10^{-3}	6.0 × 10^{-5}
Cd	1.0 × 10^{-3}	6.1	6.1	1.0 × 10^{-3}	1.0 × 10^{-5}
Ni	1.0 × 10^{-4}	-	-	2.0 × 10^{-2}	5.4 × 10^{-3}
Zn	6.0 × 10^{-4}	-	-	3.0 × 10^{-1}	1.0 × 10^{-2}
Pb	4.0 × 10^{-6}	-	-	1.4 × 10^{-3}	1.4 × 10^{-3}
Hg	6.0 × 10^{-4}	-	-	3.0 × 10^{-4}	2.1 × 10^{-5}
Cu	6.0 × 10^{-4}	-	-	4.0 × 10^{-2}	1.2 × 10^{-2}
CH_2Cl_2	1.0 × 10^{-3}	0.002	-	6.0 × 10^{-3}	-
$C_2H_4Cl_2$	1.0 × 10^{-3}	0.091	-	6.0 × 10^{-3}	-

Note: - means that there is no correlation coefficient.

Assuming that PTEs in water have a cumulative relationship with human health risks, the health risk R_T caused by a single element to two groups of people can be expressed as in Equation (9), and the total health risk HI caused by all elements in two ways to two groups of people can be expressed as in Equation (10).

$$R_T = R_i^n + R_i^c \tag{9}$$

$$H_i = \sum R \tag{10}$$

In the formula, R_i^n is the lifetime risk of health hazards caused by non-carcinogenic pollutants; ADD_i is the average daily exposure dose of threshold chemical pollutants, mg (kg × d)$^{-1}$; RfD_i is the reference dose for a certain exposure pathway of chemical pollutants, mg (kg × d)$^{-1}$; 10^{-6} is the acceptable risk level of the hypothesis corresponding to RfD.

2.5. Analytical Method of Pollution Source

2.5.1. Correlation Analysis

Correlation analysis is a statistical method for studying the uncertain relationship between variables that can be used to analyze the degree of correlation between two or more correlated variable elements. In general, if there is a positive correlation between elements, it indicates that there may be the same or similar behavior and source between elements; if it is negatively correlated, it indicates that there are different sources or no correlation between elements [39].

2.5.2. Principal Component Analysis

Principal component analysis (PCA) can use dimensionality reduction to transform the original complex and mutually contained environmental features into a few main original feature indicators that are closely related to each other. In the process of induction, as much information in the data sample should be retained as possible to ensure the reliability of the analysis results. As the basic basis for evaluating the importance of alternative indicators, the public degree of the selected indicator is closer to 1, which means that the indicator is more difficult to replace. According to Caesar's criterion, the impact factor index with an eigenvalue greater than 1 is retained as the principal component [40].

2.5.3. Positive Definite Matrix Factorization Model

The positive matrix factorization (PMF) model is a receptor model that can determine the contribution value of the pollution source to the receptor. Its application premise is that there is no value less than 0 in the source contribution matrix and the pollution source matrix, and the source contribution matrix (g_{ik}) and the source component spectrum matrix (f_{kj}) are obtained [41]. The specific calculation formula is

$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{11}$$

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{X_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right) \tag{12}$$

In the formula, X_{ij} represents the content of the jth element in the ith sample; p is the number of pollution sources; g_{ik} represents the contribution rate of source k to the first i sample; f_{kj} denotes the content of the jth element in the source k; e_{ij} is the residual matrix; Q is the objective function; n is the number of samples; m is the number of element types; u_{ij} is the uncertainty value of j element content in the ith sample.

When the element content is less than or equal to the method detection limit (MDL), u_{ij} can be calculated by Formula (13):

$$u_{ij} = \frac{5}{6} MDL \tag{13}$$

When the element content is higher than MDL, it is calculated from Formula (14) [42]:

$$u_{ij} = \sqrt{(EF \times c)^2 + \left(\frac{MDL}{2} \right)^2} \tag{14}$$

In the formula, EF is the percentage of uncertainty, and c is the measured value of the element.

2.6. Data Analysis and Mapping Tools

Microsoft Excel 2019 was used for statistical analysis of element data. Principal component analysis and correlation analysis were carried out by SPSS 26.0 and Origin2021 software, respectively, and PMF5.0 was used to analyze the source of elemental pollution. We used Origin2021 and Arcgis10.7 software to complete the drawing and editing of the map.

3. Results and Discussion

3.1. Levels of Major Parameters

A total of 22 groundwater samples were collected in this study. The PTE indicators tested included 10 indicators of As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, CH_2Cl_2 and $C_2H_4Cl_2$. The statistical results of conventional indicators of groundwater quality are shown in Table 5. According to the class III standard limit specified in the 'Groundwater Quality Standard' (GB/T 14848-2017) [29], the pH range is 3.10–7.70, with an average value of 6.54, indicating that the pH of groundwater in the study area is neutral and acidic. The content of TDS is 513.00–34,400.00 mg × L^{-1}, which indicates that the groundwater in this area is fresh water and brackish water. The variation range of TH is 342.00 mg × L^{-1}–2930.00 mg × L^{-1}, which indicates that there is a large area of high-hardness water in the groundwater in this area. The indexes of groundwater quality exceed the national class III water quality standard to varying degrees, and the most excessive index is TH.

Table 5. Statistical results of groundwater quality indicators.

Index	Detection Limit	Min	Average	Max	Standard Deviation	Coefficient of Variation
pH	-	3.10	6.54	7.7	1.19	0.18
TH (mg × L^{-1})	5	342.00	1235.19	2930	771.30	0.62
TDS (mg × L^{-1})	5	513.00	4471.59	34,400	8159	1.82
COD (mg × L^{-1})	0.5	0.95	70.9	504.6	153.04	2.48
As (mg × L^{-1})	0.005	0.00	0.02	0.05	0.02	0.85
Cd (mg × L^{-1})	0.0001	0.00	0.01	0.07	0.02	2.88
Cr (mg × L^{-1})	0.001	0.00	0.1	0.94	0.25	2.33
Cu (mg × L^{-1})	0.001	0.00	0.24	2.46	0.62	2.48
Hg (mg × L^{-1})	0.0005	0.00	0.00292	0.0049	0.00126	0.43
Ni (mg × L^{-1})	0.001	0.01	1.4	18.25	3.99	2.78
Pb (mg × L^{-1})	0.001	0.00	0.04	0.33	0.08	0.89
Zn (mg × L^{-1})	0.005	0.01	1.57	15.24	4.02	2.48
CH_2Cl_2 (mg × L^{-1})	0.005	0.00807	0.2808	1.39	0.35122	1.36
$C_2H_4Cl_2$ (mg × L^{-1})	0.0005	0.00058	0.00283	0.00911	0.00282	0.99

The distribution of PTE content in groundwater is shown in Figure 2. It can be seen from the diagram that various indicators have high outliers to varying degrees. Ni and Zn at some sites were also significantly higher. The study area is seriously polluted, and the spatial difference is large. It is necessary to evaluate the human health risk of groundwater in this area. Among the groundwater detection indicators, the coefficient of variation for Cd, Cr, Cu, Ni and Zn exceeded 1.0, indicating that there was a large difference in water quality between groundwater samples.

3.2. Groundwater Quality Evaluation Results

From the perspective of single-factor pollution in Table 6, all eight heavy metal indicators have water samples at moderate to severe pollution levels. Among them, the contribution of Ni pollution was the highest, the number of samples with severe pollution reached 14, accounting for 51.8%, and the highest value of the single-factor pollution index reached 915. Followed by Pb, four samples were at the level of severe pollution, and the highest value of the single-factor pollution index reached 32.6%. All eight indexes of ZQ01 points in all samples exceeded the standard and were at the level of heavy pollution. Except for Hg, the single-factor pollution index of the other seven indexes was at the maximum value in all samples. The second is the J1 point, which has Cr, Ni and As indicators of a heavy pollution level. From the comprehensive evaluation of groundwater indicators in Table 6, it can be seen that the quality of the groundwater environment in the study area is at a very poor level, the F value is between 7.25 and 8.49, and the drinking water wells around the accident wells are at a poor level.

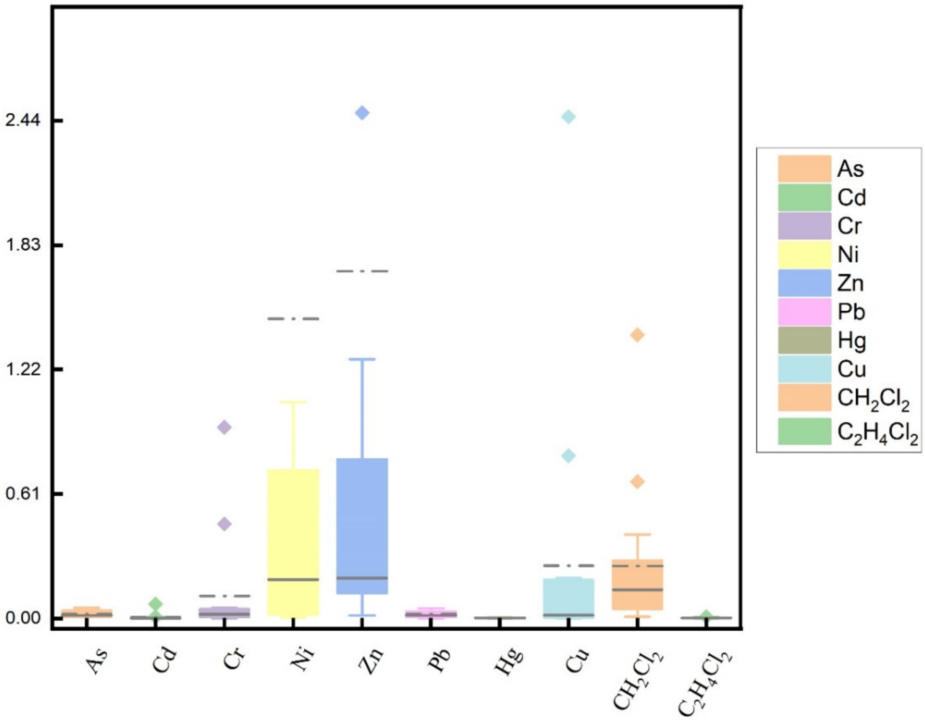


Figure 2. Distribution map of PTE content in groundwater.

Table 6. Groundwater quality evaluation table.

Analysis Index	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	F
ZQ01	10	10	10	10	10	10	10	10	8.49
ZQ02	1	3	3	6	10	10	3	3	7.88
ZQ03	0	1	0	0	0	6	3	1	7.36
ZQ04	1	1	3	1	10	1	3	1	7.61
ZQ05	0	0	0	0	0	0	1	0	7.33
ZQ06	0	0	0	0	0	1	0	0	7.24
ZQ07	1	3	3	6	0	10	1	10	7.85
ZQ08	0	1	0	0	10	10	0	1	7.62
ZQ09	0	1	0	0	0	10	0	1	7.51
ZQ10	0	0	0	0	0	1	0	0	725
ZQ11	0	0	0	0	0	1	0	0	7.25
ZQ12	0	3	1	1	10	10	3	1	7.59
ZQ13	0	3	1	6	0	10	3	6	7.73
ZQ14	0	1	0	0	0	1	0	1	7.27
ZQ15	0	3	0	0	0	10	0	1	7.59
J1	3	1	10	0	0	10	3	6	7.87
J2	0	0	3	1	0	10	0	1	7.44
J3	0	0	0	0	0	6	0	1	7.30
J4	3	0	3	0	0	10	0	1	7.39
J5	0	0	0	0	0	1	0	1	7.30
J6	3	3	3	3	0	10	3	6	7.72
J7	0	0	6	1	0	6	3	1	7.49

3.3. Groundwater Health Risk Assessment

Based on the health risk assessment model, the health risks of PTEs in groundwater in the study area to adults and children through oral intake and dermal contact were calculated as shown in Table 7. The total health risks of the five non-carcinogenic PTEs in the study area through oral intake and skin contact with the population did not exceed the maximum acceptable level recommended by the International Commission on Radiological Protection (ICRP) of 5.0×10^{-5} a^{-1}. The total health risks of the three carcinogenic heavy metal elements in the PTEs through oral intake to the population exceeded the maximum acceptable level, which should be paid attention to. From Table 7, it can be seen that Cd has the greatest carcinogenic health risk to children through oral intake, which is 9.20×10^{-4}, and Cr has the greatest carcinogenic health risk to children through skin contact, which is 7.44×10^{-5}. The maximum non-carcinogenic health risk of Ni to children through oral intake was 3.07×10^{-6}, and the maximum non-carcinogenic health risk of Zn to children through skin contact was 2.99×10^{-9}. The total non-carcinogenic risks of PTEs in groundwater to the two groups of people under the oral intake route and the skin contact exposure route were Ni > Pb > Hg > Cu > Zn and Zn > Hg > Ni > Cu > Pb, respectively. The non-carcinogenic risk of oral intake was consistent with the trend of total non-carcinogenic risk. The total non-carcinogenic risk is 1~2 orders of magnitude lower than the maximum acceptable risk level (5.0×10^{-5} a^{-1}), and the total carcinogenic risk value is 2~4 orders of magnitude higher than the total non-carcinogenic risk value, indicating that the non-carcinogenic health risk of groundwater in the study area is small, and the daily drinking water, bathing, swimming and other activities of the population will not cause significant harm.

Table 7. Health risk assessment results.

	Oral Route		**Skin Exposure**		**Comprehensive Risks**	
	Children	**Adults**	**Children**	**Adults**	**Children**	**Adults**
As	7.85×10^{-4}	5.08×10^{-4}	9.88×10^{-7}	5.81×10^{-7}	7.86×10^{-4}	5.09×10^{-4}
Cd	9.20×10^{-4}	5.96×10^{-4}	6.44×10^{-7}	3.78×10^{-7}	9.21×10^{-4}	5.96×10^{-4}
Cr	1.39×10^{-3}	8.97×10^{-4}	$7.74 \times 10-5$	4.54×10^{-5}	1.46×10^{-3}	9.42×10^{-4}
Cu	2.71×10^{-7}	2.62×10^{-7}	3.79×10^{-10}	3.32×10^{-10}	2.71×10^{-7}	2.62×10^{-7}
Hg	4.10×10^{-7}	3.96×10^{-7}	2.46×10^{-9}	2.16×10^{-9}	4.12×10^{-7}	3.99×10^{-7}
Ni	3.07×10^{-6}	2.97×10^{-6}	7.96×10^{-10}	6.98×10^{-10}	3.07×10^{-6}	2.97×10^{-6}
Pb	1.33×10^{-6}	1.29×10^{-6}	3.72×10^{-12}	3.27×10^{-12}	1.33×10^{-6}	1.29×10^{-6}
Zn	2.37×10^{-7}	2.30×10^{-7}	2.99×10^{-9}	2.62×10^{-9}	2.40×10^{-7}	2.32×10^{-7}
CH_2Cl_2	1.29×10^{-5}	8.38×10^{-6}	—	—	1.29×10^{-5}	8.35×10^{-6}
$C_2H_4Cl_2$	6.46×10^{-6}	4.18×10^{-6}	—	—	6.46×10^{-6}	4.18×10^{-6}

The EPA's acceptable risk level for carcinogens is in the range of 10^{-6}–10^{-4}. Less than 10^{-6} indicates that the risk is not obvious, 10^{-6}–10^{-4} indicates that there is a risk, and more than 10^{-4} indicates that there is a significant risk. From Table 7, it can be seen that Cr has the greatest health risk of carcinogenicity for children through both routes. The carcinogenic risk of oral intake is 1.39×10^{-3}, which exceeds the acceptable risk level by 1–3 orders of magnitude, with a significant risk. The carcinogenic risk of skin contact is 7.74×10^{-5}. The carcinogenic risks of CH_2Cl_2 and $C_2H_4Cl_2$ in PTEs to children through oral intake were 1.29×10^{-5} and 6.46×10^{-6}, respectively, which were risky but not significant. As, Cd and Cr have a significant risk to both groups under the exposure route of oral intake, and the risk is not obvious under the exposure route of skin contact. The carcinogenic risk of oral intake is 2–4 orders of magnitude larger than that of skin contact. Therefore, As, Cd and Cr are the three primary factors that cause the carcinogenic health risk of the population (especially children) in this area. We should pay attention to the pollution of As, Cd and Cr in the groundwater in the study area.

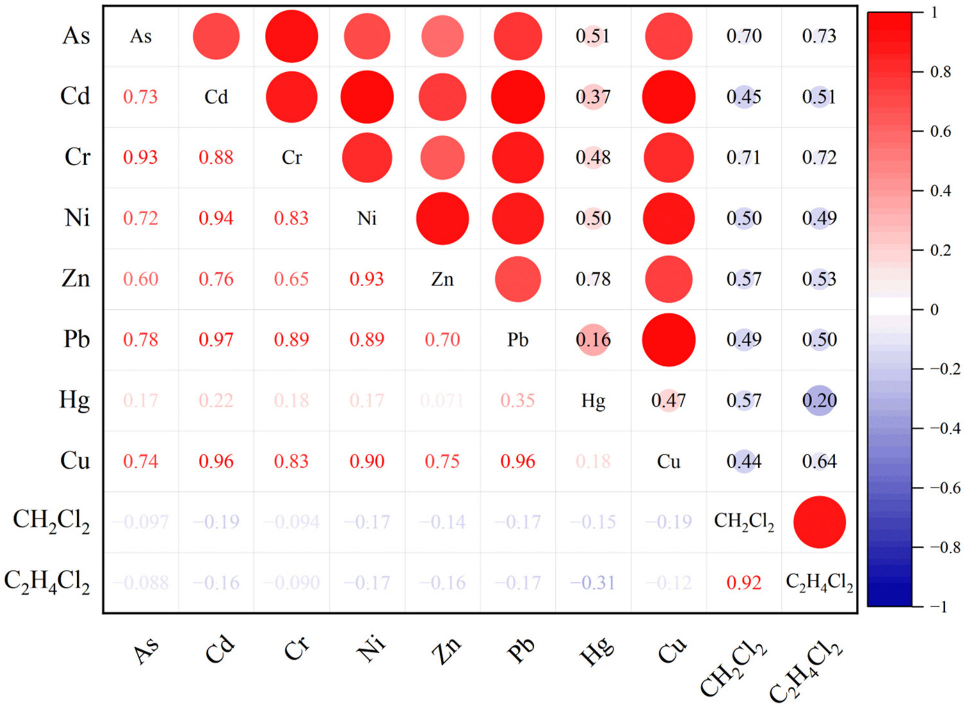
In general, by comparing the health risks of groundwater PTEs to the two groups of people in different exposure routes, it can be seen that the health risks of children and adults are in the same order of magnitude, whether through oral intake or skin contact, but children are always slightly higher than adults. Therefore, we should focus on the health risks of groundwater PTE toxicity to children.

3.4. Source Apportionment of Elements in Groundwater

3.4.1. Correlation Analysis

Correlation analysis has a basic distinguishing effect on exploring the sources of different PTEs, and can simply identify the correlation between different PTEs. In general, correlation analysis can be used to analyze whether different PTEs have a significant positive correlation, so as to determine whether different PTEs may come from similar sources or the same source [43].

In this paper, the correlation between groundwater PTEs in the study area was analyzed by Origin2021 software (Figure 3).



Siginficant level: 0.05

Figure 3. Correlation analysis matrix.

The results show that there is a significant positive correlation between the seven heavy metal elements except Hg in the study area, and the correlation is pairwise, indicating that there may be an information overlap between As, Cd, Cr, Cu, Ni, Pb and Zn elements in groundwater in the study area, and the correlation coefficients are all > 0.5, so they may undergo the same environmental geochemistry or have a compound pollution relationship. However, the correlation coefficient between $C_2H_4Cl_2$ and CH_2Cl_2 is 0.92, which is a very significant correlation level but has no significant relationship with other PTEs. Therefore, CH_2Cl_2 and $C_2H_4Cl_2$ are more likely to come from the same pollution source. In addition, there is no obvious correlation between Hg and other PTEs in the study area, and there may be independent pollution sources.

3.4.2. PCA

The results of the KMO and Bartlett sphericity tests showed that the KMO test value was 0.652, the Bartlett sphericity test statistic was 0, and the significance test value of the Bartlett sphericity test was $p < 0.05$, indicating that this group of data was suitable for PCA. PCA was carried out by IBM SPSS Statistics 26.0 software. Three principal components were extracted by the Kaiser standardized orthogonal rotation method, which were F1, F2 and F3.

Three principal components (F1–F3) were extracted by principal component analysis and could explain 89.454% of the total variance. The principal component loads contained in each component are shown in Table 8. The contribution of As, Cd, Cr, Cu, Ni, Pb and Zn in F1 is higher, and the absolute value of the factor load exceeds 0.8. The principal component contains seven heavy metal elements. The long-term input of livestock and poultry manure and the application of chemical fertilizers may be the main sources of Cu, Zn, Cd and Cr in the study area. Livestock feed additives, pesticides and fertilizers are used more frequently in the local area [44,45], indicating that they are mainly affected by agricultural sources. The contribution of CH_2Cl_2 and $C_2H_4Cl_2$ in F2 is higher, and the factor load is greater than 0.9. Since some indicators of groundwater have changed significantly due to the dumping of chemical waste by three enterprises in the study area, F2 explains the impact of this pollution incident on groundwater quality, indicating that it may be affected by anthropogenic industrial sources. The factor load of Hg in F3 is greater than 0.8, and Hg is seriously polluted in some sample points. However, due to the volatility of Hg, its content has a large degree of spatial dispersion. It is preliminarily judged that Hg enrichment is mainly caused by the accumulation of micro-particles released by surrounding coal combustion through atmospheric deposition, which is mainly an industrial sedimentation source.

Table 8. The main calculation results of PTEs' principal component analysis.

HM	F1	F2	F3
As	0.843	0.135	0.037
Cd	0.969	0.038	−0.02
Cr	0.924	0.13	0.009
Cu	0.952	0.061	−0.052
Hg	0.281	−0.298	0.899
Ni	0.959	0.055	−0.109
Pb	0.968	0.022	0.214
Zn	0.827	0.06	−0.219
CH_2Cl_2	−0.185	0.92	0.26
$C_2H_4Cl_2$	−0.209	0.949	0.045
Eigenvalue	6.104	1.884	0.957
Variance explained rate (%)	61.045	18.838	9.572

3.4.3. PMF

Principal component analysis combined with correlation analysis basically explained the possible sources of 10 PTEs in the study area. On this basis, the PMF method can be used to quantitatively analyze the source of PTEs in the study area. When calculating the uncertainty of PTEs, the signal-to-noise ratio of Ni and Zn is small (S/N = 0), which is classified as 'Bad', the signal-to-noise ratio of Cu is small (S/N < 0.5), which is classified as 'weak', and the remaining PTEs are classified as 'strong'. After trial calculation, when the number of setting factors is 2–7, the number of operations is 25 times and the number of factors is 3, Q_{Robust}/Q_{true} decreases rapidly, and the residual value is between −3 and 3. The proportion is the largest, indicating that the correlation between the measured value and the predicted value of the PMF model is high [46], and it is inferred that there are three main sources of PTEs in this area.

According to the source composition spectrum (Figure 4) and source contribution diagram (Figure 5), it was found that As, Cd, Cr, Cu and Pb had higher loads on PMF1, which were 34%, 88%, 54.7%, 93.1% and 38.2%, respectively, which were consistent with the results of F1. Cd, as a representative element of PMF1, is an iconic element of agricultural activities [47]. Agricultural activities such as industrial waste, pesticides, fertilizers and plastic film use will lead to its high content. The excessive point of the Cd element is distributed near villages and towns in the study area, which also confirms this point. In the study area, there is the Minggao No. 2 coal mine, which is located in the east of the Jidong coalfield. There are many roadways filled with water. Some studies have pointed out that As, Ni and Cr are relatively stable in nature. They are usually regarded as crustal elements, mainly derived from soil characteristics [48]. Therefore, PMF1 is mainly affected by agricultural sources.

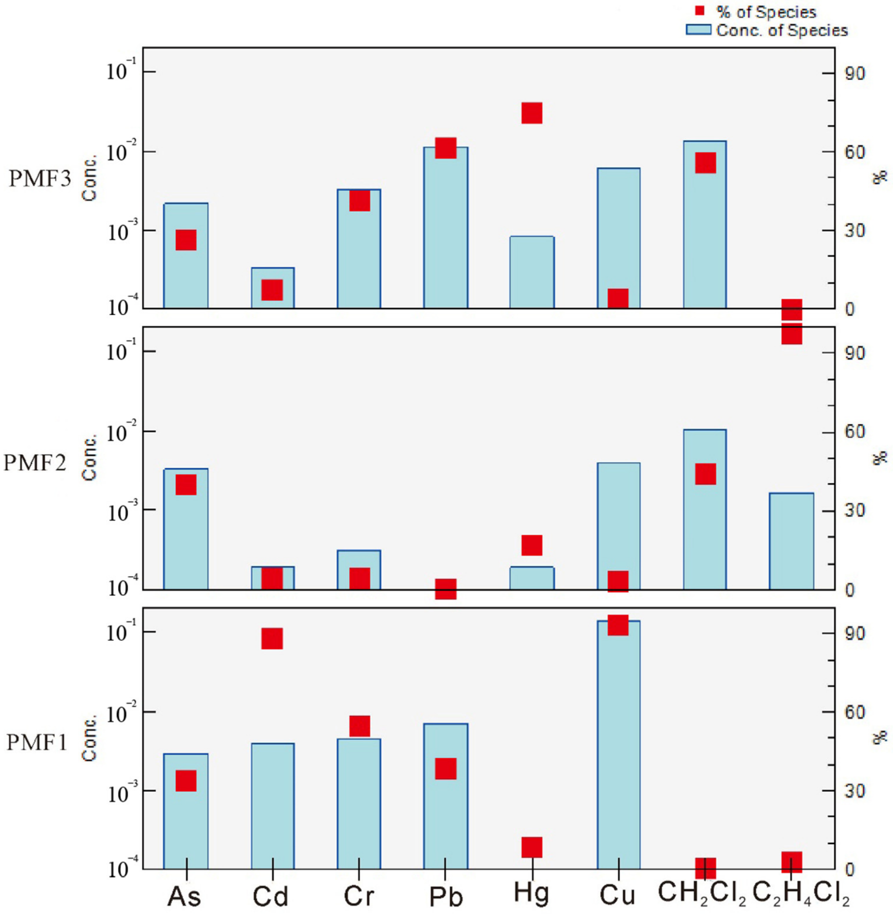


Figure 4. Analytical results of PMF model.

The contribution rates of CH_2Cl_2 and $C_2H_4Cl_2$ in PMF2 were 43.9% and 97.6%, respectively, indicating that the load of similar elements was higher, which was due to the fact that the surrounding companies poured waste samples into the accident well, mainly due to the influence of artificial industrial sources.

PMF3 has higher Hg and Pb element loads, with contribution rates of 74.7% and 61.8%. Atmospheric deposition and surface water are the main sources of Hg. Chemical enterprises use oil and coal as the main fuel, and coal combustion leads to the emission of Hg-containing gases. Pb is the iconic element of traffic activity [49], the main source of automobile exhaust and coal combustion, so it suggests that Hg enrichment is mainly due to its release into the surrounding metallurgy and coal, mainly from industrial sedimentation sources.

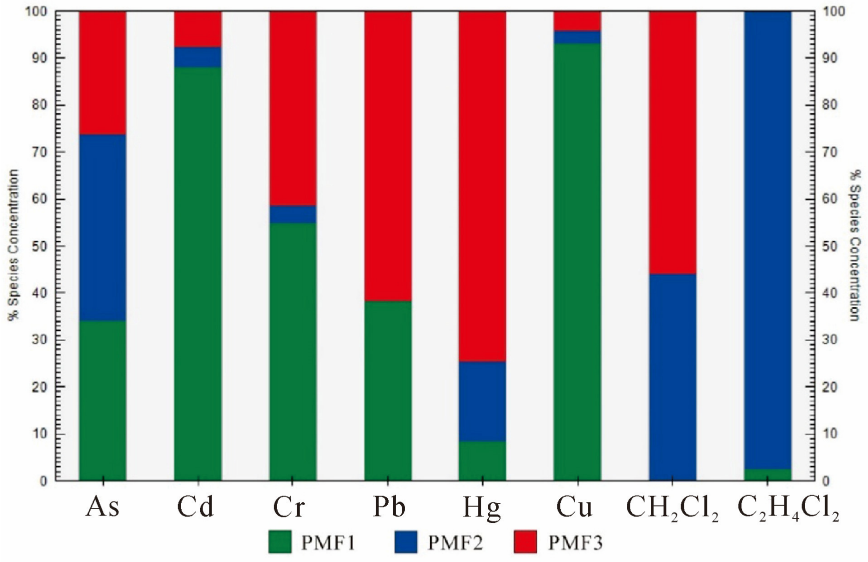


Figure 5. The proportion of PTE factors in groundwater.

From the source apportionment results, the two analyses have similar identification results in the qualitative identification of potential pollution sources and generally represent the same potential pollution sources. In addition, the two models are slightly different in the distribution of principal component composition but do not affect the overall analytical results. From the perspective of the contribution rate of pollution sources, the trend and contribution rate of pollution sources analyzed by the two models are different. The reason for this difference is that the factorization process of the two models is different, that is, although both of them are based on the calculation of the least squares method, they are different in the factor extraction model [50,51].

According to the factor profile of PMF, the average contribution of sample sources to the total mass was calculated (Figure 6). The results showed that As, Cd, Cr, Cu and Pb are mainly from agricultural sources, with a contribution rate of 39.84%. CH_2Cl_2 and $C_2H_4Cl_2$ are mainly affected by anthropogenic industrial sources, with a contribution rate of 26.13%. Hg is from an industrial sedimentation source, with a contribution rate of 34.04%.

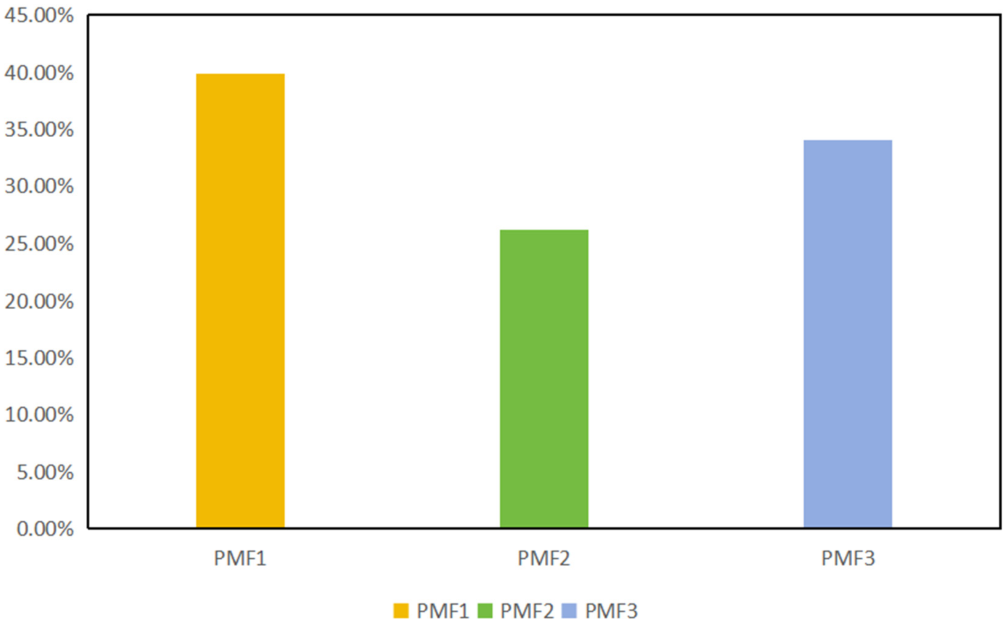


Figure 6. Contribution rate distribution diagram of sources.

4. Conclusions

This paper took an accident site in Zhangqiu City, Shandong Province, as the main research area, determined the pollution situation and pollution source of the research area, made a pollution assessment and health risk assessment of the research area, and provided information for the sustainable development and utilization of groundwater resources in the research area and on the protection of and improvement in the living environment. It is of great significance. The comprehensive indexes of pH, TDS, COD, TH and PTEs in groundwater at the accident site are significantly high, exceeding the class III standard limit to varying degrees, and the spatial dispersion of PTE content is large. The single-factor pollution index values of Ni and Pb in the PTE index are high. According to the single-factor pollution index method, most of the PTEs are at a safe or alert level. According to the Nemerow comprehensive pollution index, there are heavy pollution levels. The sample points are ZQ01 and ZQ07, and Ni is the main contribution factor in the region. In view of the comprehensive consideration of PTEs, the groundwater in the study area is seriously polluted. According to the non-carcinogenic risk assessment, the total non-carcinogenic risk index of groundwater around the accident site for nearby children and adults does not exceed the non-carcinogenic safety risk value, but the risk value for children is higher than that for adults. According to the carcinogenic risk assessment, the carcinogenic health risk values of adults and children exposed to As, Cd and Cr through oral intake in the study area are all high, and the maximum acceptable risk value is 1.0×10^{-4}. The control of As, Cd and Cr in groundwater in the study area should be strengthened. Among the two exposure routes, the oral intake route has the greatest impact. On the basis of correlation analysis and principal component analysis, combined with the PMF model, the main pollution sources of PTEs in the study area were determined. As, Cd, Cr, Cu, Ni, Pb and Zn are from agricultural sources (PMF1), CH_2Cl_2 and $C_2H_4Cl_2$ are from human-made industrial sources (PMF2) and the accumulation of Hg is mainly from industrial sedimentation sources (PMF3). The contribution rates of the three pollution sources were 39.84%, 26.13% and 34.04%, respectively.

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