

## Research Article

# Groundwater Quality Evaluation for Potable Use and Associated Human Health Risk in Gaobeidian City, North China Plain

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The groundwater in Gaobeidian city is used for drinking, irrigation, industrial production, and other purposes. With the rapid development of the economy and urbanization, groundwater quality has been seriously affected. The main purposes of this paper are to evaluate the groundwater quality in the study area on the basis of understanding the hydrochemical characteristics of the study area and assess the possible health risks of groundwater to children and adults. In this paper, the entropy weight method was used to determine the weight of each evaluation parameter, and on this basis, groundwater quality evaluation was carried out, and the spatial distribution map of groundwater quality was drawn according to the evaluation results. The results show that the weight values of the five parameters of  $\text{NO}_2^-$ , Fe, As,  $\text{Cr}^{6+}$ , and  $\text{NO}_2\text{-N}$  are more than 0.1 among the total of fifteen parameters, and the concentration of these five parameters can be considered as the main influencing parameters of groundwater quality. The calculation results of the entropy weighted water quality index (EWQI) show that all the groundwater quality in the study area is class 1 water, which is Excellent Water. However, the EWQI value is the highest in the southwest of the study area, showing a trend of deterioration of groundwater water quality. Since all groundwater samples were evaluated as “excellent water,” it was speculated that the natural environment had more influence on groundwater chemical characteristics than human factors. The study found that 7.407% and 55.556% of the water samples posed a noncarcinogenic health risk to adults and children, respectively. The main responsible parameters for noncarcinogenic risk are  $\text{F}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{Cr}^{6+}$ . The carcinogenic risk for adults ranged from 0 to  $6.91\text{E-}04$ , with a mean of  $1.00\text{E-}04$ . The carcinogenic risk for children ranged from 0 to  $1.03\text{E-}03$ , with a mean of  $1.55\text{E-}04$ . These toxic elements are mainly from industries. Therefore, the deterioration of groundwater quality can be prevented by strengthening the sewage management of various industries.

## 1. Introduction

The water resource is one of the most important natural resources on the Earth, and it is an important basis for human life and production [1]. However, with the deepening of the development and utilization of water resources, especially under the serious shortage of freshwater resources in China and similar areas in the world, the deterioration of groundwater quality has become a major problem [2]. Groundwater resources have been paid increasing attention by scholars at home and abroad, and their status has become more and more important [3, 4]. Over the past few decades, China has

experienced rapid industrialization and urbanization, accompanied by a massive increase in waste and wastewater, and it poses a serious threat to the availability and quality of groundwater. The quality of groundwater is closely related to human health, and the use of contaminated groundwater will pose significant health risks to human beings. Therefore, it is crucial to carry out water quality assessment and health risk assessment of groundwater resources.

At present, there are many methods of water quality evaluation, such as fuzzy mathematics method, membership degree method, factor analysis method, grey modeling method, artificial neural network, and water quality index

method. Each method has its own advantages and disadvantages, such as fuzzy mathematics method for a comprehensive evaluation, and can fully reflect the quality of groundwater, objectively calculate the membership degree of each parameter relative to the standard limit, and effectively avoid the human influence, but the calculation process is too complex. In recent years, some data-driven methods, such as neural network and projection pursuit technology, are rarely used in groundwater quality assessment due to the insufficient expression of water quality information [5]. The water quality index is considered to be the most effective method to evaluate water quality [6]. However, in the process of water quality index calculation, the weight of each parameter is usually given by experts according to experience, which is highly subjective and easy to lose the information of some characteristic parameters in the region. The water quality index improved by the entropy weight method effectively solves the problem of subjective weighting [7]. Therefore, this method of groundwater quality assessment is widely used in the world [8–10]. In addition to the traditional water quality assessment, there are some assessments on health risks caused by exposure to pollution [11, 12]. Most of these health risk assessment studies are based on the risk assessment model proposed by the US Environmental Protection Agency (USEPA). This paper uses the existing health risk assessment system in China to determine the possible risk of groundwater to human health in the research area [13].

Gaobeidian is located in the central part of the North China Plain. The importance of groundwater is self-evident in Hebei Province, which suffers from severe water shortages. Therefore, there are a lot of researches on groundwater quality. Zhou et al. used various methods to study the chemical characteristics of groundwater in Xinle City, Shijiazhuang, the capital of Hebei Province, and evaluated the water quality of drinking and irrigation and concluded that  $\text{Na}^+$  pollution mainly came from industrial pollution. Zhou et al. used the mate-element extension analysis model of entropy weight to evaluate the quality of groundwater for drinking water and irrigation and its health risks in Gu'an of the North China Plain. They believed that the water quality in the study area was generally good, but there was a high risk of noncancer for children. In this paper, Gaobeidian, a key county in Hebei Province, was selected as the research area to study the chemical characteristics of shallow groundwater in the region, and to this basis, the groundwater quality assessment and groundwater human health risk assessment were carried out. The rationality and visualization of the evaluation results are the focus of this paper. Groundwater quality assessment is a part of environmental assessment. Common groundwater quality assessment methods include the single factor index method, the Nemerow index method, and the fuzzy mathematics evaluation method. Each method has its own advantages and disadvantages [14]. In this paper, the entropy weight method is adopted to evaluate groundwater quality by the improved WQI method. This method has been proved to be an effective method for groundwater quality evaluation. The likelihood of a water pollution event threatening human and ecosystem health and the degree of adverse effects over time can be calculated using the human health risk assessment methodology [15, 16]. This paper

focuses on the calculation of health risks caused by common contaminants in groundwater and conducts health risk assessments for children and adults.

The main purposes of this study are to understand the basic characteristics of hydrogeochemistry in the study area on the basis of mathematical statistical methods, to carry out the assessment of underground water quality by using the EWQI method, and finally to carry out the risk assessment of human health. On the basis of the above research, we can deepen the understanding of the influence of groundwater on human health to promote the prevention and control of groundwater pollution, strengthen the reasonable monitoring of groundwater resources, and provide suggestions for the rational development and utilization of groundwater.

## 2. Study Area

Gaobeidian is located at the eastern foot of Taihang Mountain, northeast of Baoding City, Hebei Province, along the Beijing-Guangzhou Railway. It is located in the center of three large cities: Beijing, Tianjin, and Baoding. The geographical location is from  $39^{\circ}05'45''$  to  $39^{\circ}23'28''$  north latitude and from  $115^{\circ}47'00''$  to  $116^{\circ}12'28''$  east longitude. Gaobeidian has a superior geographical location, convenient transportation conditions, and obvious regional advantages.

Located in the alluvial plain of the eastern piedmont of Taihang Mountain in the northern part of the North China Plain, Gaobeidian City has a warm temperate semihumid monsoon climate with distinct four seasons and remarkable climatic characteristics. From 1956 to 2017, the average precipitation was 522.20 mm [17]; the annual average temperature was  $12.2^{\circ}\text{C}$ ; and the annual average sunshine duration was 2,575.3 h. The western part of Gaobeidian is the edge zone of the alluvial fan at the eastern foot of Taihang Mountain, which is mainly composed of loam soil. The eastern part is a fluvial alluvial plain, which is the result of the dual action of two kinds of alluvial deposits. The deep part of the soil layer is the extension of the western diluvial alluvial fan, and the upper part is covered by the modern fluvial deposits. The terrain is flat, and the soil texture is more complex than in the west. The terrain slopes from northwest to southeast with an altitude of 40.4–10.9 m. The terrain slopes from east to west 1/1,500–1/1,700 and from south to north 1/3,000–1/3,600. The terrain is relatively flat. From the perspective of landforms, Nanjuma River has two terraces: the first-class terraces are hard to distinguish from the floodplain, but on the scour bank side of the river, the first-class terrace is missing, forming a steep wall, and only the second-class terrace remains.

The geological tectonic system of Gaobeidian belongs to the second subsidence zone of the Neocathaysian tectonic system. The working area is located in the plain area. According to the years of drilling data, the urban area is all Quaternary Holocene, alluvial and diluvial formations.

*Holocene system:* the buried depth of the bottom plate is between 10 and 30 m. The lithology is mainly alluvial silt and silty clay mixed with fine sand and silt, and the thickness is less than 40 m.

*Pleistocene*: the buried depth of the bottom plate is between 50 and 135 m, thickness is 50–150 m, and lithology is alluvial clay, alluvial lacustrine clay, silty clay, silt with medium fine sand, and silt.

*Middle Pleistocene*: it is the stratum of flood and alluvial origin. The lower part is brownish-red, the local part is yellowish-brown sandy clay with fine silt, the thickness is 100 m, and the buried depth of the bottom boundary is 90–300 m.

*Lower Pleistocene*: the buried depth of the bottom plate is between 140 and 420 m, and thickness is 100–200 m. The lithology is mainly moraine glacial water deposits, alluvial diluvial clay, alluvial lacustrine clay, silty clay with sand, gravel, and sand layers.

### 3. Materials and Methods

**3.1. Sample and Sample Description.** In this study, a total of 27 shallow water samples were obtained. The sampling sites are shown in Figure 1. The water samples were mainly taken from pumped wells. Water samples were taken, sealed, and transported in strict accordance with the national technical regulations [18]. A total of 26 physical and chemical indicators of groundwater samples were determined. Field test indicators included pH, chromaticity, turbidity, visible matter, smell, and taste. Major ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ), total hardness (TH), total dissolved solids (TDS), fluoride ( $\text{F}^-$ ), nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), nitrate nitrogen ( $\text{NO}_3^-$ -N), nitrite nitrogen ( $\text{NO}_2^-$ -N), metallic ions ( $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cr}^{6+}$ ), and nonmetallic ions (As,  $\text{I}^-$ ) were measured in the laboratory. The samples were collected in sterilized polythene bottles, and each bottle was required to be rinsed with distilled water before collection. After collection, the bottles were air-tight, labeled, and transported to the laboratory immediately. The latitude and longitude of each sampling point were recorded by a GPS at the site.  $\text{Na}^+$  and  $\text{K}^+$  concentrations were measured using flame photometry, whereas  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ , and  $\text{Cl}^-$  concentrations were determined using titration.  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations were measured by ion chromatography, whereas  $\text{NO}_2^-$  concentrations were measured by ultraviolet-visible photometry. pH was measured using a pH meter, while a conductivity analyzer was used to measure TDS. The sampling method, sampling procedures, and sample conservation and analysis were performed following national standard methods for drinking water quality [19]. The precision and accuracy of the data have been examined by calculating the charge balance errors (within  $\pm 5\%$ ) and the recovery ratio (within  $\pm 10\%$ ) [20].

**3.2. Entropy Weighted Water Quality Index (EWQI).** There are many methods to determine the weight, which can be divided into three categories: subjective weighting method, objective weighting method, and integrated weighting method. The subjective weighting method generally includes the subjective experience method, subjective

index queuing classification method, expert survey method, and so on. The objective weighting method generally includes entropy weighting method, deviation and mean square deviation method, and multiobjective programming method, which determines the weight by certain mathematical methods according to the relationship between the original data. The result of weighting does not depend on the subjective judgment of human beings and has strong mathematical theoretical basis.

In this paper, the entropy weight method was used to evaluate the groundwater quality by the improved WQI method. The entropy weight method is to use the tool of information entropy to calculate the weight of each index, which can reduce the error caused by neglecting the weight and provide a basis for the comprehensive evaluation of multiple indexes.

The entropy weight method is an objective weighting method. The calculation process is very complex, and the following steps need to be followed. In the first step, assuming that there are  $m$  water samples to evaluate the water quality ( $i = 1, 2, \dots, m$ ), each water sample has  $n$  parameters to be evaluated ( $j = 1, 2, \dots, n$ ). According to the observation data, the original matrix of each evaluation index of various points is constructed as follows [21]:

$$X_{ij} = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1n} \\ x_{21} & x_{22} & & x_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ x_{m1} & x_{m2} & \cdots & x_{mn} \end{bmatrix}, \quad (1)$$

where  $X_{ij}$  represents the observed data of the  $j^{\text{th}}$  evaluation parameters of the  $i^{\text{th}}$  groundwater sample. Then the data is preprocessed, and the original matrix is normalized to obtain the normalized judgment matrix. The reason for normalization is to eliminate the influence caused by the difference of different units and orders of magnitude of characteristic indicators. The normalized constructor is constructed by the following equation:

$$y_{ij} = \frac{x_{ij} - (x_{ij})_{\min}}{(x_{ij})_{\max} - (x_{ij})_{\min}}. \quad (2)$$

After transformation, the normalized judgment matrix is obtained as follows:

$$Y_{ij} = \begin{bmatrix} y_{11} & y_{12} & \cdots & y_{1n} \\ y_{21} & y_{22} & & y_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ y_{m1} & y_{m2} & \cdots & y_{mn} \end{bmatrix}. \quad (3)$$

Then the ratio of the index value of the  $j^{\text{th}}$  index to the index value of the  $i^{\text{th}}$  sample is calculated by the following equation:

$$P_{ij} = \frac{y_{ij}}{\sum_{i=1}^m y_{ij}}. \quad (4)$$

The entropy of the evaluation index is determined according to the definition of entropy and the evaluation indexes of various points. The information entropy is expressed as follows:

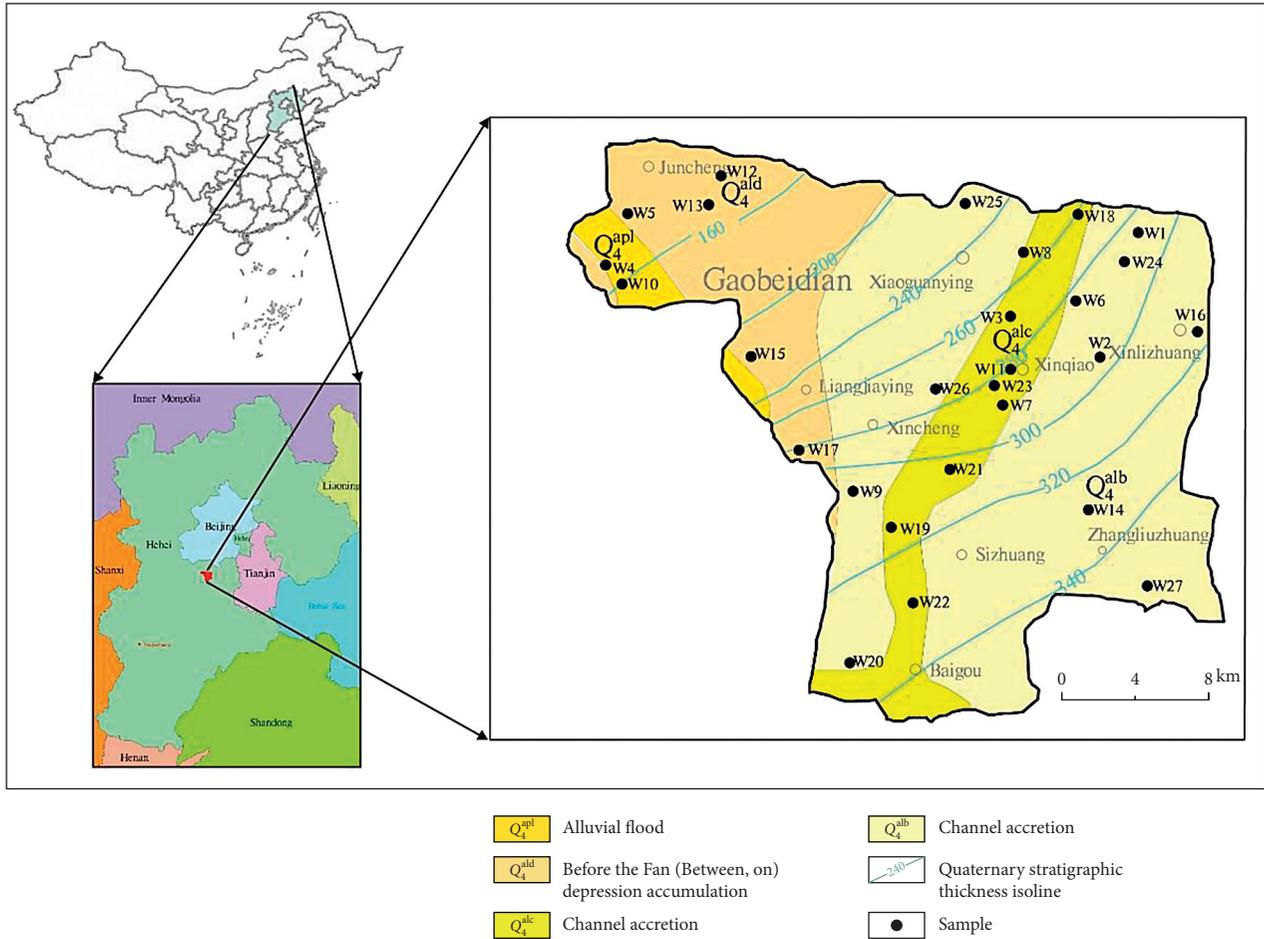


FIGURE 1: Location of the study area and monitoring wells.

$$e_j = \frac{1}{\ln m} \sum_{i=1}^m P_{ij} \ln P_{ij}. \quad (5)$$

The smaller the value of  $e_j$ , the greater the influence of  $j$  index. The entropy weight can be calculated as follows:

$$w_j = \frac{1 - e_j}{\sum_{j=1}^n (1 - e_j)}, \quad (6)$$

where  $w_j$  is defined as the entropy weight of the  $j$ th parameter. The second step in calculating the EWQI is to assign a quality rating table  $q_j$  to each parameter.  $q_j$  can be calculated by the following equation:

$$q_j = \frac{C_j}{S_j} \times 100, \quad (7)$$

where  $C_j$  is the concentration of each chemical parameter in each water sample, the unit is mg/L;  $S_j$  is the limit value of all physical and chemical parameters in China Groundwater Quality Standard for potable groundwater, and the unit is mg/L. It can be seen from the above equation that if the concentration of parameter  $j$  in the groundwater sample is 0,

then  $q_j$  is also 0. When the concentration of parameter  $j$  is just the allowable value,  $q_j$  is 100.

The EWQI can be calculated in the third step by the following equation:

$$EWQI = \sum_{j=1}^n w_j q_j. \quad (8)$$

**3.3. Health Risk Assessment.** Groundwater poses health risks to human health mainly through drinking and skin contact. Health risk assessment evaluates the harmful effects of exposure to chemicals in the contaminated environment on humans. Differences in evaluation coefficients arise because of the different physiological conditions of children and adults. This study calculated health risks due to contaminants in groundwater and evaluated health risk assessment in children and adults. The risks of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , Fe,  $\text{Cr}^{6+}$ , Mn, As, and  $\text{F}^-$  were considered in this study.

The noncarcinogenic risk from drinking contact is as follows [22]:

$$\text{Intake}_{\text{oral}} = \frac{C \times IR \times EF \times E D}{BW \times AT}, \quad (9)$$

$$HQ_{\text{oral}} = \frac{\text{Intake}_{\text{oral}}}{RfD_{\text{oral}}}, \quad (10)$$

where  $\text{Intake}_{\text{oral}}$  is the average daily dose of oral intake route (mg/(kg·d)).  $C$  and  $IR$  represent the concentration of pollutants in groundwater (mg/L) and the daily ingestion rate of water (L/day), respectively.  $EF$ ,  $ED$ ,  $BW$ , and  $AT$  are defined as the exposure frequency (day/a), the exposure duration (a), average body weight (kg), and average exposure time (day), respectively.  $HQ_{\text{oral}}$  and  $RfD_{\text{oral}}$  are noncarcinogenic hazard quotients and reference doses, respectively, through the oral intake route.

The noncarcinogenic risk from skin contact is calculated as follows [23]:

$$\text{Intake}_{\text{dermal}} = \frac{DA \times EV \times SA \times EF \times E D}{BW \times AT}, \quad (11)$$

$$DA = K \times C \times t \times CF, \quad (12)$$

$$SA = 239 \times H^{0.417} \times BW^{0.517}, \quad (13)$$

$$HQ_{\text{dermal}} = \frac{\text{Intake}_{\text{dermal}}}{RfD_{\text{dermal}}}, \quad (14)$$

$$RfD_{\text{dermal}} = RfD_{\text{oral}} \times ABS_{gi}, \quad (15)$$

where  $\text{Intake}_{\text{dermal}}$  is the average daily dose of dermal intake route (mg/(kg·d)),  $DA$  is the exposure dose (mg/cm<sup>2</sup>), and  $SA$  represents skin contact area (cm<sup>2</sup>).  $EV$  is the daily exposure frequency,  $K$  is skin permeability (0.001 cm/h).  $CF$ ,  $t$ ,  $H$ , and  $ABS_{gi}$  represent a conversion factor, contact duration, average height, and the parameter for gastrointestinal absorption, respectively [24].

The total noncarcinogenic risk is expressed as follows:

$$H_i = HQ_{\text{oral}} + HQ_{\text{dermal}}, \quad (16)$$

$$HI_{\text{total}} = \sum_{i=1}^n HI_i, \quad (17)$$

where  $HI$  is a risk index.  $HI$  represents  $HQ$  with two or more exposure pathways,  $HQ$  is for multiple substances, and two or more exposure pathways can be expressed as  $HI$ . When  $HQ$  and  $HI$  exceed 1, residents are considered at noncarcinogenic risk [25].

Carcinogenic factors represent the human carcinogenic risk of groundwater in a certain area, which refers to the possibility that residents may get cancer from drinking and using groundwater.  $\text{Cr}^{6+}$  and  $\text{As}$  were the major carcinogens in the study area. The carcinogenic risk of this ion can be calculated as follows:

$$CR_{\text{oral}} = \text{Intake}_{\text{oral}} \times SF_{\text{oral}}, \quad (18)$$

$$CR_{\text{dermal}} = \text{Intake}_{\text{dermal}} \times SF_{\text{dermal}}, \quad (19)$$

$$SF_{\text{dermal}} = \frac{SF_{\text{oral}}}{ABS_{gi}}, \quad (20)$$

$$CR_{\text{total}} = CR_{\text{oral}} + CR_{\text{dermal}}, \quad (21)$$

where  $CR$  and  $SF$  represent the risk of cancer and the slope factor of carcinogenic pollutants. According to the regulations of the Ministry of Environmental Protection of China, the limit of  $CR$  is  $10^{-6}$ . The  $SF_{\text{oral}}$  value of  $\text{Cr}^{6+}$  is 0.5 (mg/(kg d)), and the  $SF_{\text{oral}}$  value of  $\text{As}$  is 1.5 (mg/(kg d)) [26].

## 4. Results and Discussion

**4.1. Descriptive Statistics of Groundwater Physical and Chemical Parameters.** This paper analyzes the statistical characteristics of groundwater physical and chemical parameters, including minimum, maximum, and median values. Descriptive statistics of groundwater physical and chemical parameters are shown in Table 1. It can be seen from Table 2 that the pH value ranges from 7.64 to 8.43, with an average value of 8.01. It can be seen that the pH value of most groundwater samples is greater than 7, so it can be considered that the shallow groundwater in the study area is weakly alkaline. The near-neutral pH values (7.64–8.43) are characteristic of waters in a carbonate system, indicating that the dissolved carbonates are predominant in the source. The TDS concentration ranged from 277.76 to 778.62 mg/L, with an average of 467.63 mg/L. Because the TDS concentration of the groundwater samples was not higher than 1 g/L, the groundwater in the study area belonged to freshwater. The total hardness (TH) of the samples ranged from 89.07 to 429.48 mg/L, and the TH concentration in 34.78% of the samples was higher than that in Quality Standards for Groundwater of China (QSGC). The cations involved in this paper mainly include  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ , and the anions involved mainly include  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{NO}_3^-$ .  $\text{Ca}^{2+}$  concentration ranged from 22.04 to 94.99 mg/L, with an average of 54.78 mg/L. In the groundwater in the study area, the highest concentration of trace elements is Sr, which is 1.179 mg/L, followed by Mn, Fe,  $\text{Cr}^{6+}$ , and As.

**4.2. Hydrochemical Characteristics of Groundwater.** The hydrochemical types of groundwater are helpful in understanding the genetic conditions of natural water [27]. The Piper diagram, which is a graphical method, is used to analyze the hydrochemical characteristics of groundwater [28, 29]. Based on the data of the major ions, a Piper diagram was drawn, as shown in Figure 2. The ions are expressed in milliequivalents per liter (mg/L). It can be found from the Piper diagram that the main anions in this region are carbonic acid;  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are the main cations affecting the hydrochemical types in this region; and  $\text{Na}^+$  also accounts for a high proportion. In other words, as can be seen from the figure, the main hydrochemical types in this area are Ca·Mg– $\text{HCO}_3$  and Mg·Ca– $\text{HCO}_3$ .

According to the hydrochemical types of the water samples, the spatial variation diagram of the chemical types

TABLE 1: Descriptive statistics of concentrations of groundwater parameters.

Item	Min	Max	Average	Sd	Nation standards
K <sup>+</sup>	0.300	1.100	0.656	0.262	—
Na <sup>+</sup>	8.800	181.300	48.694	36.180	200.000
Ca <sup>2+</sup>	22.044	94.990	54.776	18.741	—
Mg <sup>2+</sup>	8.266	67.101	32.551	16.086	—
HCO <sub>3</sub> <sup>-</sup>	214.056	712.311	352.352	108.600	—
CO <sub>3</sub> <sup>2-</sup>	0.000	14.273	1.145	3.452	—
Cl <sup>-</sup>	2.852	93.458	28.456	26.849	250.0
SO <sub>4</sub> <sup>2-</sup>	6.200	132.400	43.006	36.574	250.0
F <sup>-</sup>	0.000	2.615	0.595	0.566	1.50
NO <sub>3</sub> <sup>-</sup>	0.480	44.100	8.369	11.051	88.600
NO <sub>2</sub> <sup>-</sup>	0.000	0.088	0.008	0.019	3.000
Fe	0.000	0.161	0.022	0.042	0.300
As	0.000	0.002	0.000	0.001	0.010
Mn	0.000	0.455	0.093	0.133	0.100
Sr	0.000	1.179	0.572	0.293	—
Cr <sup>6+</sup>	0.000	0.026	0.003	0.007	0.050
TH	89.071	429.480	270.819	92.453	450.0
TDS	277.759	778.615	467.627	157.071	1000.000
pH	7.640	8.430	8.012	0.177	6.5–8.5
I <sup>-</sup>	0.000	0.078	0.032	0.027	0.080
NO <sub>3</sub> -N	0.000	9.960	1.568	2.624	20.000
NO <sub>2</sub> -N	0.000	0.270	0.017	0.054	1.000

TABLE 2: Classification standards of groundwater quality according to EWQI.

Rank	EWQI value	WQI class
1	<50	Excellent
2	50–100	Good
3	100–150	Medium
4	150–200	Poor
5	>200	Extremely poor

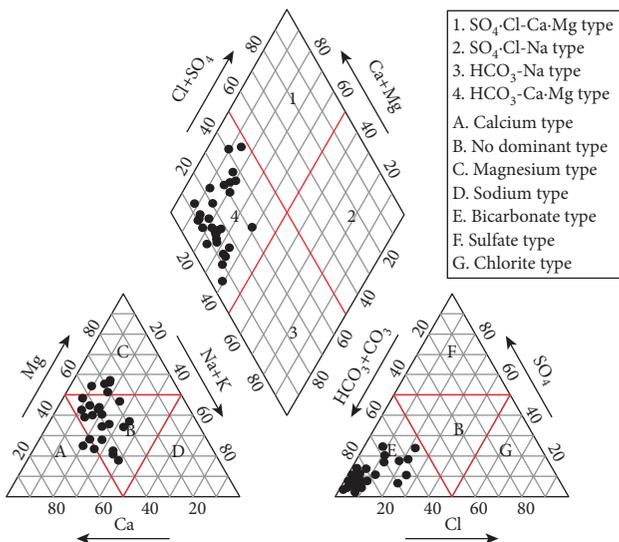


FIGURE 2: Piper map of the shallow aquifer.

of shallow groundwater in the study area was drawn, as shown in Figure 3. It can be seen from the diagram that the groundwater chemical type has obvious horizontal zoning

from west to east in this area. At the piedmont alluvial fan area, the aquifer particles are coarse. The hydrochemical type is single, mainly bicarbonate type [30]. Along the flow path, hydrochemical type transits from Ca•Mg-HCO<sub>3</sub> to Mg•Ca-HCO<sub>3</sub>, Ca•Na-HCO<sub>3</sub>, and then to Na•Mg-HCO<sub>3</sub> type.

The groundwater data were plotted in the Gibbs diagram (Figure 4). Gibbs diagram can reflect the relationship between TDS and  $c(\text{Na}^+)/c(\text{Na}^++\text{Ca}^{2+})$  and between TDS and  $c(\text{Cl}^-)/c(\text{Cl}^-+\text{HCO}_3^-)$ . Gibbs diagram can be used to intuitively determine the main factors affecting the chemical formation of groundwater and trace the origin mechanism of various ions [31] and can trace the origin mechanism of various ions [32], including filtration, evaporation and concentration, and meteoric precipitation [33].

According to Gibbs diagram of groundwater in the study area, the  $c(\text{Na}^+)/c(\text{Na}^++\text{Ca}^{2+})$  range is 0.1–0.6, and the  $c(\text{Cl}^-)/c(\text{Cl}^-+\text{HCO}_3^-)$  range is 0~0.5. The water sample points are all located in the left-center part of the Gibbs map, and it is speculated that the groundwater in this region is mainly affected by leaching. The minerals in the aquifer of this region are mainly carbonate and silicate, with a small amount of calcareous clay minerals locally. The concentration of HCO<sub>3</sub><sup>-</sup> is relatively high because it is mainly affected by filtration.

**4.3. Entropy Weighted Water Quality Index.** Although 22 physical and chemical parameters in 27 groundwater samples were tested in this paper, the limits of K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, and Sr<sup>2+</sup> were not included in the evaluation parameters of groundwater water quality due to the lack of limits of K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, and Sr<sup>2+</sup> in QSGC.

In this paper, 15 parameters were selected to evaluate the groundwater quality, and EWQI was determined as the focus of this study by using entropy weight and groundwater sample quality ranking based on QSGC. The calculated results of weights and information entropy of each index obtained by the above steps are shown in Table 3. It can be seen from the table that the weights of five parameters, NO<sub>2</sub><sup>-</sup>, Fe, As, Cr<sup>6+</sup>, and NO<sub>2</sub>-N, are more than 0.1, while the weights of other parameters are less than 0.1. It can be considered that the concentration of these five parameters is the main influencing parameter of groundwater quality.

EWQI values of each water sample can be obtained through calculation, and the calculated results are shown in Table 4. It can be seen that among the 27 water samples in total, the EWQI values range from 3.13 to 48.66, with an average value of 14.97. All the calculated EWQI values are within the range of class 1 groundwater. This indicates that the groundwater in the study area has been well protected and has not been polluted. However, there is still a trend of groundwater quality deterioration in some areas. For example, Sizhuang Town and Baigou Town, located in the southwest of Gaobeidian City, have the highest EWQI values, both exceeding 45 [34]. Through investigation, it was found that there are industrial enterprises such as tanneries and bag processing plants in the area. In the process of reproduction, these factories will discharge sewage, which

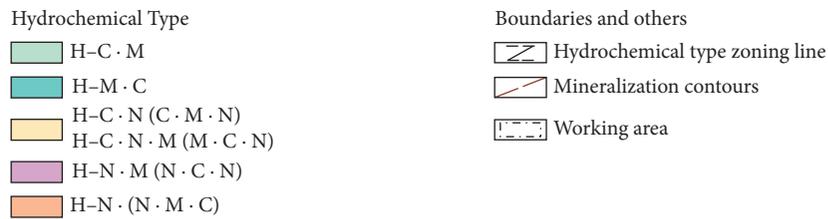
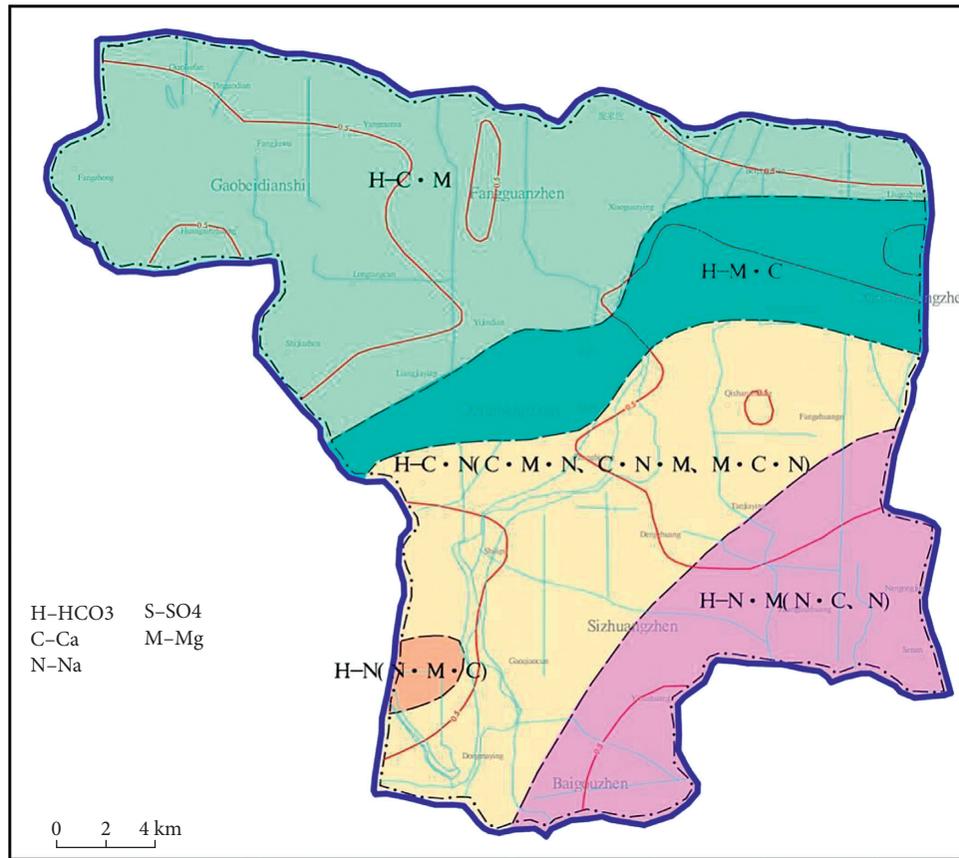


FIGURE 3: Spatial variation in groundwater hydrochemical type of the shallow groundwater.

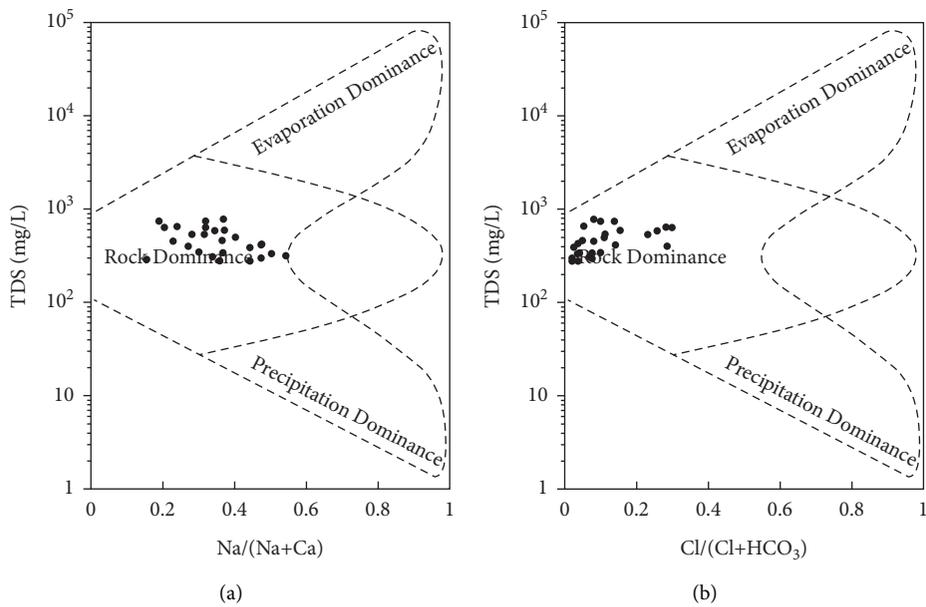


FIGURE 4: Gibbs diagram of the shallow groundwater.

TABLE 3: Entropy weight of hydrochemical parameters.

Item	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	F <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	Fe	As
Information entropy, $e_j$	0.889	0.849	0.867	0.829	0.772	0.525	0.582	0.531
Entropy weight, $w_j$	0.028	0.038	0.033	0.043	0.057	0.119	0.105	0.118
Item	Mn	Cr <sup>6+</sup>	I <sup>-</sup>	TH	NO <sub>3</sub> <sup>-</sup> -N	NO <sub>2</sub> <sup>-</sup> -N	TDS	
Information entropy, $e_j$	0.746	0.585	0.861	0.955	0.679	0.372	0.971	
Entropy weight, $w_j$	0.064	0.104	0.035	0.011	0.080	0.158	0.007	

TABLE 4: Assessment results according to computed EWQI.

Sample ID	WQI	Rank
w1	3.418	1
w2	8.928	1
w3	12.266	1
w4	7.964	1
w5	5.858	1
w6	10.518	1
w7	9.427	1
w8	7.729	1
w9	15.445	1
w10	11.870	1
w11	3.131	1
w12	6.196	1
w13	11.450	1
w14	16.331	1
w15	4.673	1
w16	13.675	1
w17	6.462	1
w18	10.845	1
w19	48.658	1
w20	21.182	1
w21	30.317	1
w22	47.314	1
w23	32.833	1
w24	13.447	1
w25	19.404	1
w26	7.711	1
w27	17.144	1

will infiltrate into the groundwater. Although it has not caused pollution to the groundwater, there is a trend of water quality deterioration, so the monitoring and management of groundwater should still be strengthened.

By comparing the above hydrochemical zoning maps, it can be seen that the chemical types of groundwater gradually evolved from HCO<sub>3</sub>-Ca•Mg type in the northwest to HCO<sub>3</sub>-Na•Ca type in the southeast, and the concentration of Na<sup>+</sup> in the groundwater environment gradually increased in the direction of groundwater flow, while the concentration of Ca<sup>2+</sup> gradually decreased.

In order to make the calculation results of EWQI more intuitive display, Surfer software was used to interpolate according to the results and make the contour map. The results are shown in Figure 5. Because the groundwater in the study area is considered to be less polluted by human activities, it is speculated that the groundwater quality in the southwest of the study area is slightly worse than that in other areas, which is mainly due to natural factors [3]. First of all, alternating cation adsorption may have occurred because according to the type of water chemistry, it can be seen that the concentration of Na<sup>+</sup>

increases, while the concentration of Ca<sup>2+</sup> decreases, so it is speculated that this is the reason for alternating cation adsorption. Secondly, minerals from the surrounding rock enter the groundwater under leaching. However, the topography of the study area is relatively flat; the hydraulic slope is small; the groundwater contacts with the surrounding rock minerals for a long time; and various chemical components in the groundwater are easy to form accumulation. In addition, some chemical components are not easy to precipitate from the groundwater, leading to higher and higher concentrations. The groundwater quality calculated by EWQI also gradually worsens along the direction of groundwater flow from northwest to southeast, which may be related to the chemical evolution of groundwater in the above natural and environmental conditions [35].

To sum up, although all the groundwater quality in the study area is class I water, there is still a trend of deterioration of regional groundwater quality, such as Sizhuang Town and Baigou Town in the southwest of Gaobeidian City. In order to further explore the impact of groundwater on human health, a human health risk assessment will be carried out below.

**4.4. Health Risk Assessment.** The results of the noncarcinogenic risk assessment in the study area are shown in Table 5. The minimum  $HI_{oral}$  value of shallow groundwater sample is 0.158; the maximum is 3.421; and the average value is 0.546. There were two sample sites for adults in the study area with  $HI_{oral}$  higher than 1, that is, 7.407% of the study sites were above the acceptable limit. For shallow underground water samples in the study area, the  $HI_{oral}$  range of adults is 0.158 to 1.601, and that of children is 0.337 to 3.421, indicating that the water in the area will affect both adults and children.

The spatial distribution of noncarcinogenic risks in shallow groundwater in the study area (Figure 6) reveals significant health risks for children and adults in shallow groundwater in the western and southern regions. Clearly, noncarcinogenic health risks cover a much larger area for children than for adults.

The spatial distribution of noncarcinogenic risks in shallow groundwater in the study area reveals significant health risks for children and adults in shallow groundwater in the western and southern regions. Clearly, noncarcinogenic health risks cover a much larger area for children than for adults.

Combined with the data in the study area (Figure 7), it can be concluded that for adults, the main factor affecting health risk assessment is F<sup>-</sup>. In addition, NO<sub>3</sub><sup>-</sup>, Mn, As, and

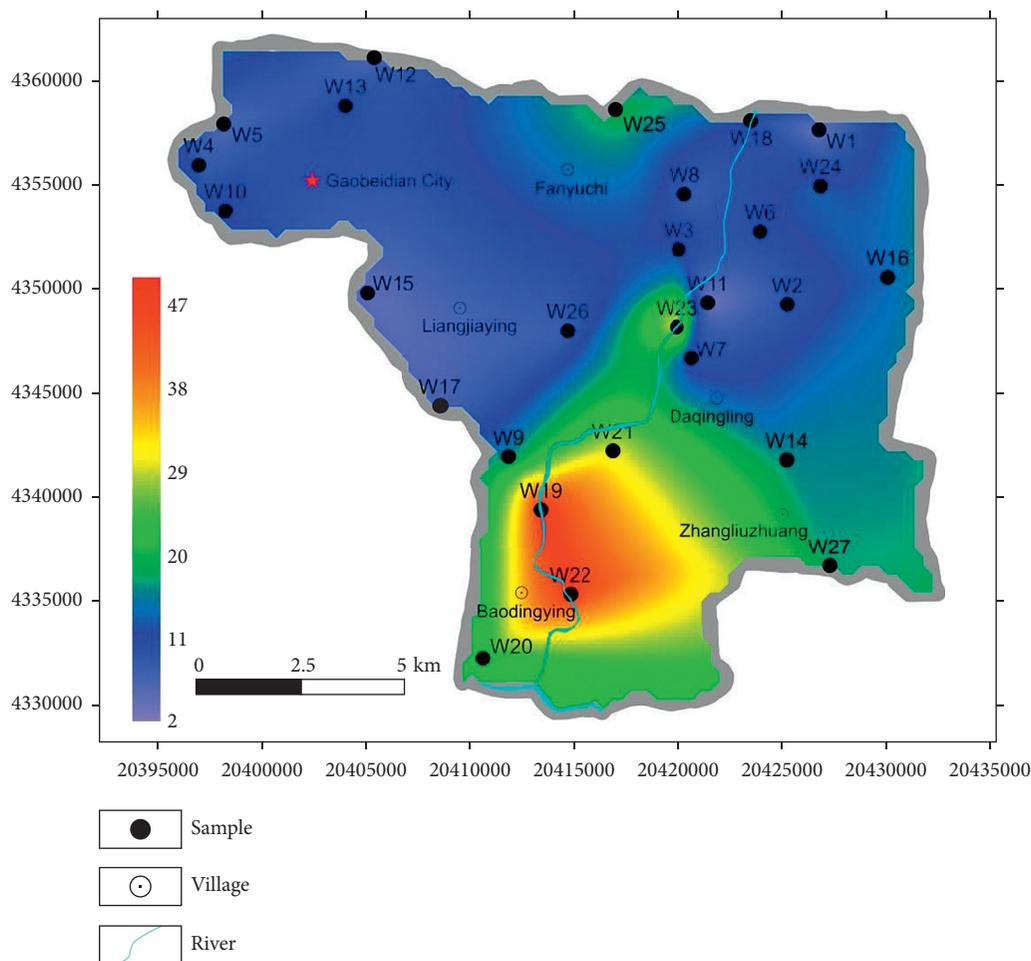


FIGURE 5: Spatial distribution of groundwater quality of the shallow aquifer.

TABLE 5: Human noncarcinogenic and carcinogenic health risks in the groundwater.

Sample	Noncarcinogenic risk		Carcinogenic risk	
	Children	Adult	Children	Adult
W1	0.378	0.204	$1.98E-04$	$1.33E-04$
W2	0.567	0.265	$7.12E-05$	$3.33E-05$
W3	0.715	0.334	$7.12E-05$	$3.33E-05$
W4	<b>1.308</b>	0.655	$3.17E-04$	$2.13E-04$
W5	0.649	0.304	0	0
W6	0.965	0.452	$7.12E-05$	$3.33E-05$
W7	0.708	0.331	0	0
W8	<b>1.040</b>	0.626	$1.03E-03$	$6.91E-04$
W9	<b>2.048</b>	<b>1.050</b>	$6.73E-04$	$4.52E-04$
W10	<b>1.920</b>	0.974	$5.54E-04$	$3.72E-04$
W11	0.405	0.217	$1.98E-04$	$1.33E-04$
W12	0.756	0.354	0	0
W13	0.623	0.292	0	0
W14	<b>1.215</b>	0.569	0	0
W15	0.824	0.434	$3.56E-04$	$2.39E-04$
W16	<b>1.013</b>	0.474	0	0
W17	<b>1.005</b>	0.519	$3.56E-04$	$2.39E-04$
W18	0.979	0.458	$7.12E-05$	$3.33E-05$
W19	<b>3.421</b>	<b>1.601</b>	0	0
W20	0.337	0.158	0	0

TABLE 5: Continued.

Sample	Noncarcinogenic risk HI		Carcinogenic risk CR	
	Children	Adult	Children	Adult
W21	<b>1.539</b>	0.720	0	0
W22	<b>2.065</b>	0.967	<b>1.42E-04</b>	<b>6.67E-05</b>
W23	<b>1.734</b>	0.812	0	0
W24	0.644	0.301	0	0
W25	0.686	0.321	<b>8.55E-05</b>	<b>4.00E-05</b>
W26	0.899	0.421	0	0
W27	<b>1.983</b>	0.928	0	0

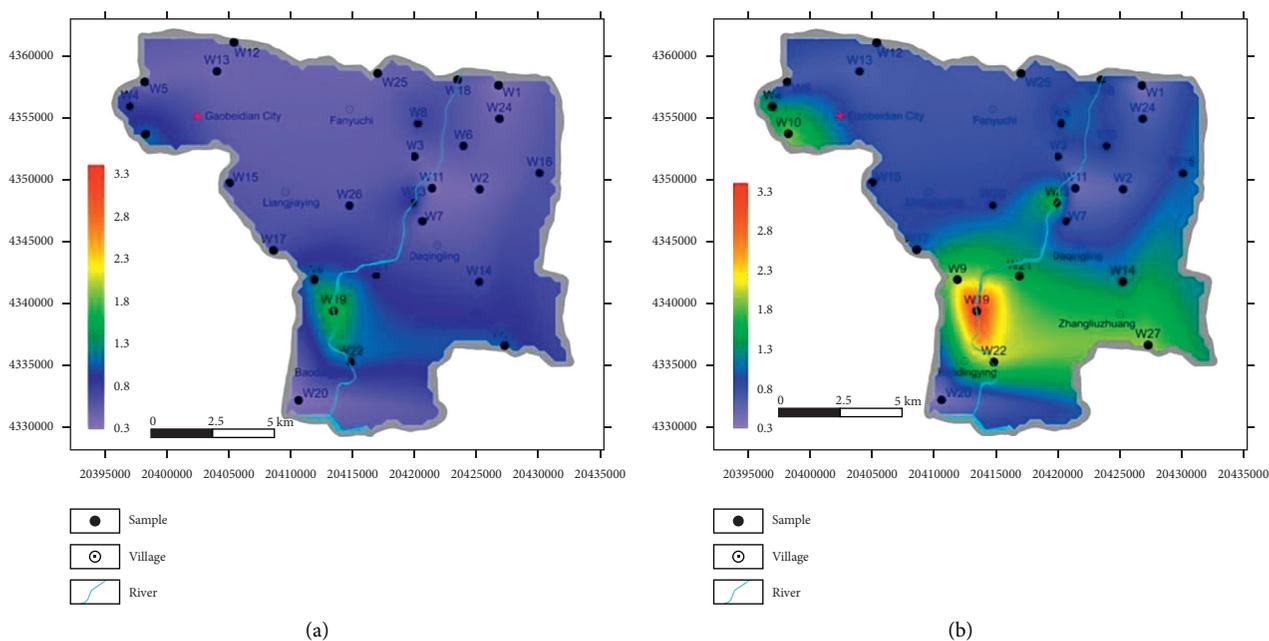


FIGURE 6: Spatial zonation of noncarcinogenic risk for adults and children.

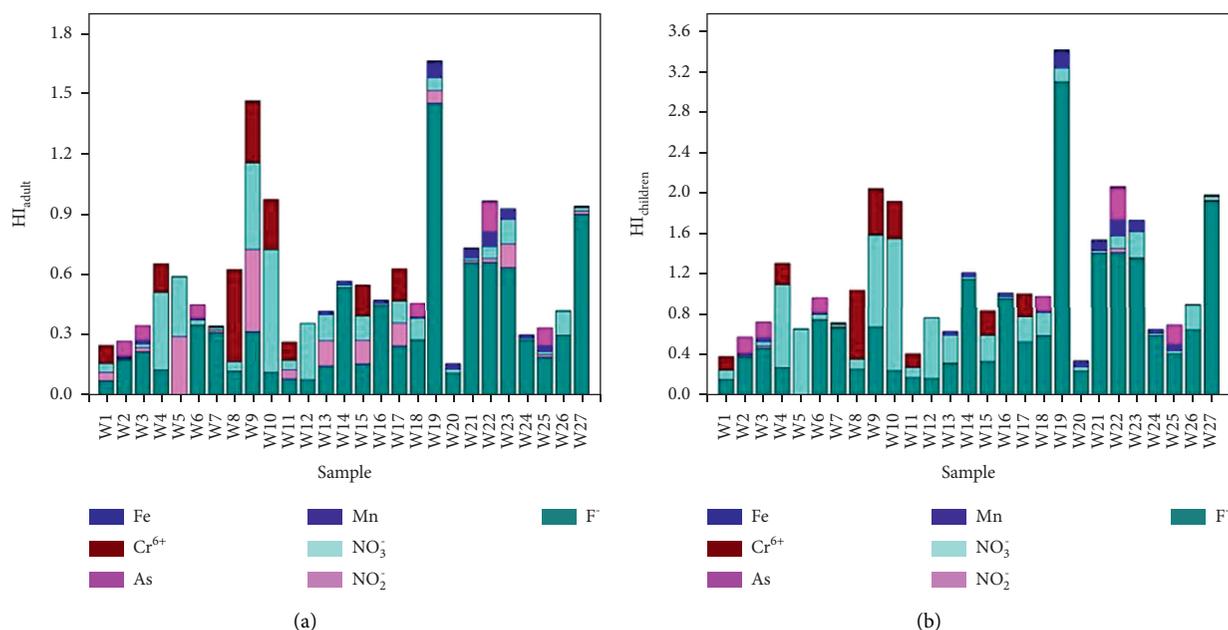


FIGURE 7: Noncarcinogenic risk of the groundwater samples for adults and children.

TABLE 6: Carcinogenic risk of Cr<sup>6+</sup> and As in all the samples.

Sample	Cr <sup>6+</sup>		As	
	Children	Adult	Children	Adult
W1	1.98E-04	1.33E-04	0	0
W2	0	0	7.12E-05	3.33E-05
W3	0	0	7.12E-05	3.33E-05
W4	3.17E-04	2.13E-04	0	0
W5	0	0	0	0
W6	0	0	7.12E-05	3.33E-05
W7	0	0	0	0
W8	1.03E-03	6.91E-04	0	0
W9	6.73E-04	4.52E-04	0	0
W10	5.54E-04	3.72E-04	0	0
W11	1.98E-04	1.33E-04	0	0
W12	0	0	0	0
W13	0	0	0	0
W14	0	0	0	0
W15	3.56E-04	2.39E-04	0	0
W16	0	0	0	0
W17	3.56E-04	2.39E-04	0	0
W18	0	0	7.12E-05	3.33E-05
W19	0	0	0	0
W20	0	0	0	0
W21	0	0	0	0
W22	0	0	1.42E-04	6.67E-05
W23	0	0	0	0
W24	0	0	0	0
W25	0	0	8.55E-05	4.00E-05
W26	0	0	0	0
W27	0	0	0	0

Cr<sup>6+</sup> are also responsible for adult health risks [36]. At the same time, many scholars have suggested that these factors are responsible for the higher health risks in many regions. Therefore, some measures should be taken to control the pollution and reduce the content of NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Mn, As, and Cr<sup>6+</sup> so as to reduce the health risk of shallow groundwater to the personnel in the study area.

As can be seen from Figure 7, W14, W19, W21, W22, W23, and W27, F<sup>-</sup> has the greatest influence, so it is necessary to pay attention to the source of F<sup>-</sup>. According to the investigation in the study area, the high content of F<sup>-</sup> may not only be caused by the interaction between fluorite and groundwater and the leaching of F<sup>-</sup> in groundwater, which causes pollution to groundwater and thus affects human health. The main reason may be the pollution of the groundwater in the study area caused by the luggage manufacturing enterprises in the related area.

For children, the risk of NO<sub>3</sub><sup>-</sup> ions in groundwater in W10 exceeds 1, which poses a noncarcinogenic health risk. The concentration of NO<sub>3</sub><sup>-</sup> at this point is 44.1 mg/L. The concentration of W9 NO<sub>3</sub><sup>-</sup> in the water sample site was 30.93 mg/L, and the risk at this point was close to 1, which also resulted in a certain degree of noncarcinogenic health risk. According to the understanding of the study area, the higher concentration of NO<sub>3</sub><sup>-</sup> may be caused by agricultural pollution.

The results show that the shallow groundwater along the river in the southwest of the study area is a significant health risk, which is consistent with the results of EWQI.

The results of carcinogenic risk assessment in the study area are shown in Table 6

Data show that the carcinogenic risk of adults ranges from 0 to 6.91E-04, with an average value of 1.00E-04, and some regions exceed the limit of 3.33 to 69.13 times. The carcinogenic risk of children ranged from 0 to 1.03E-03, with an average value of 1.55E-04, and some water samples exceeded the limit by 7.12–102.96 times. Groundwater in the region poses the greatest cancer risk to children, followed by adults. Children in the same area are more likely to develop cancer than adults because of their lower body weight and greater skin exposure [37].

The spatial distribution of cancer risk for adults (Figure 8) indicates that the areas of high cancer risk for children and adults are consistent. The major health risks of shallow groundwater are mainly distributed in the north and west of the study area, mainly concentrated in Heping Office of Gaobeidian City, Xiaoguaning Town and some areas of Xincheng Town, which are the areas with high carcinogenic risk of shallow groundwater. According to the understanding of the research area, there are leather tanneries, luggage processing enterprises, and other industries in Xiaoguaning Township and Xincheng Town. A certain amount of sewage containing Cr<sup>6+</sup> will be discharged in the production process, and the surface sewage will pollute the groundwater through infiltration. Polluting enterprises, such as cement plants near the Heping Office, will produce sewage containing Cr<sup>6+</sup>, which will pollute the groundwater. As can be seen from Figures 9 and 10, the arsenic content of

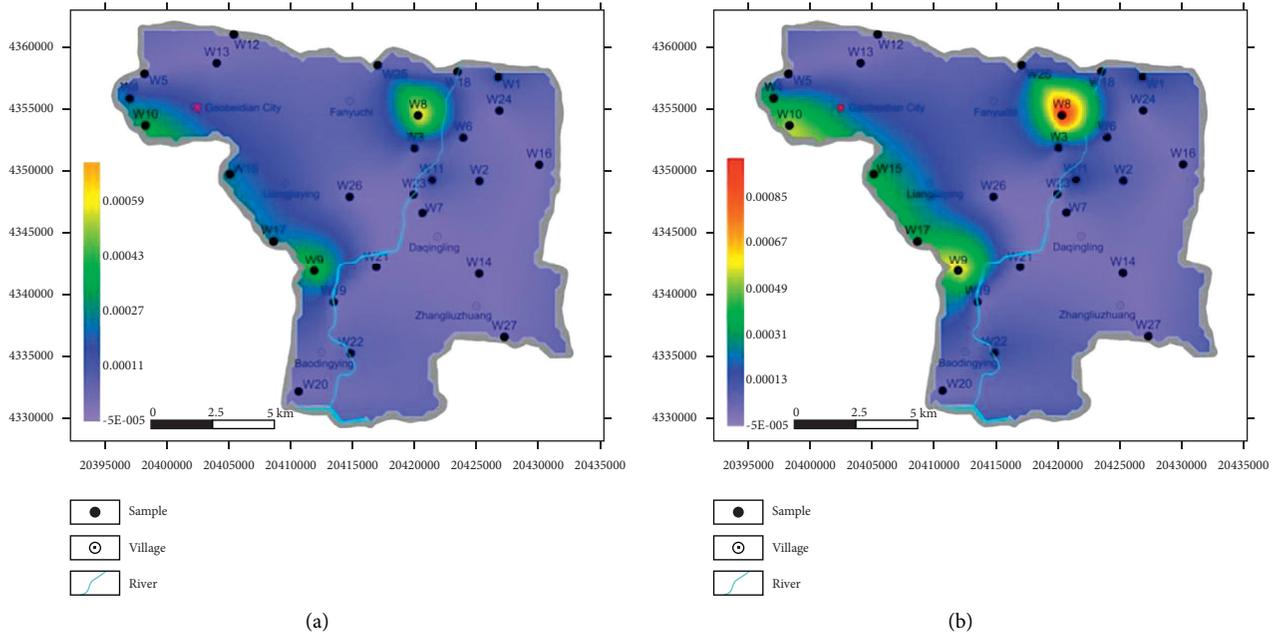


FIGURE 8: Carcinogenic risk of the groundwater samples for adults and children.

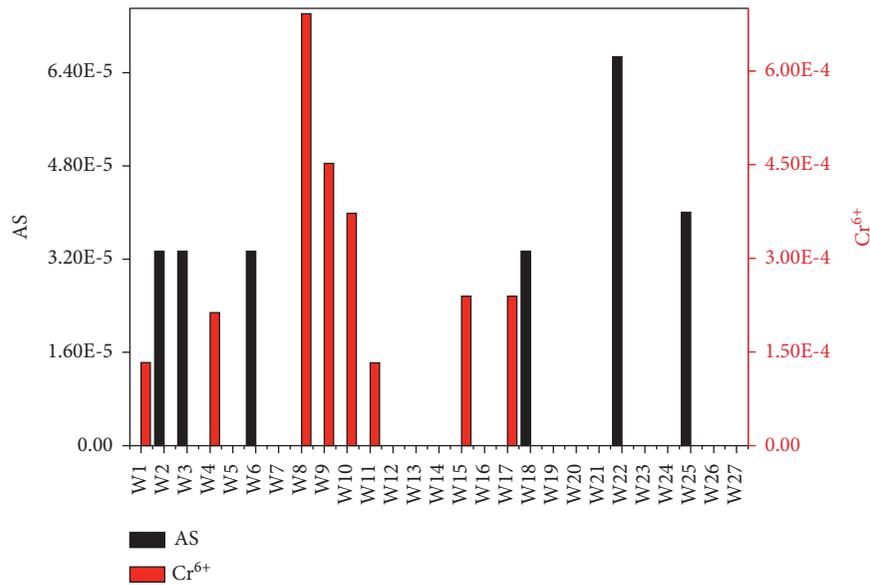


FIGURE 9: Carcinogenic risk of the groundwater samples for adults.

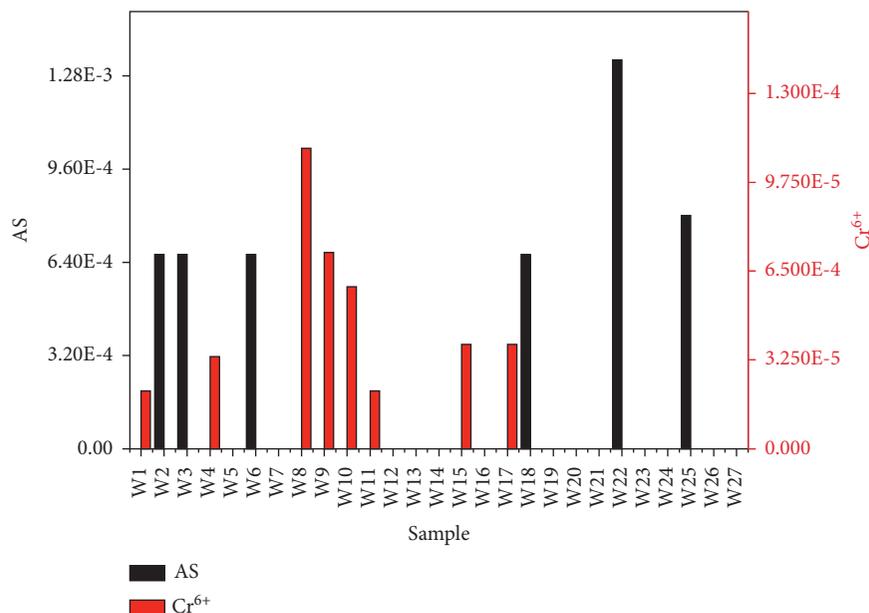


FIGURE 10: Carcinogenic risk of the groundwater samples for children.

W22 and W25 is relatively high. After analysis, it may be caused by the groundwater pollution caused by the related enterprises that manufacture bags and suitcases. The use and drinking of groundwater by local residents poses a significant risk of cancer.

From the discussion above, although the region has better water quality and is suitable for drinking and irrigation, it still poses certain risks to human health, especially for children, with both carcinogenic and noncarcinogenic risks being higher. In addition, as the average value of IR, ED, BW, and AT is taken in the calculation process, pollutants such as pesticides are not taken into account, so the risk assessment is still uncertain to some extent. Nevertheless, groundwater pollution is still a problem that needs to be paid attention to.

## 5. Conclusions

Groundwater is the main source of drinking water and industrial water in Gaobeidian. In this paper, 26 indicators of groundwater samples from 27 monitoring wells in the study area were tested, and their basic characteristics were analyzed through the description and statistical analysis [38]. EWQI method is used to evaluate groundwater quality, and the factors that may affect groundwater chemistry and water quality are discussed in detail. Health risks were assessed in the study area. To provide local decision-makers with groundwater protection and management measures with a view to achieving more rational monitoring and exploitation of groundwater.

The shallow groundwater in Gaobeidian is weakly alkaline and has low TDS content, which belongs to freshwater. The abundance of cations in the study area is  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$ , and the abundance of anions is  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{CO}_3^{2-}$ , respectively. From west to east in the study area, the groundwater hydrochemical types vary from

simple to complex. From the zoning map of shallow groundwater hydrochemical types, it can be seen that the groundwater hydrochemical types show certain zoning in the horizontal direction [39]. The hydrochemical types of shallow groundwater in the study area can be mainly divided into four types:  $\text{HCO}_3\text{-Ca}\cdot\text{Mg}$  type and  $\text{HCO}_3\text{-Mg}\cdot\text{Ca}$  type in the recharge area,  $\text{HCO}_3\text{-Ca}\cdot\text{Na}$  type in the transition area, and  $\text{HCO}_3\text{-Na}\cdot\text{Ca}$  type in the discharge area [40].

The improved EWQI method was used to evaluate the groundwater quality in the study area. By calculating the weight value of the five parameters of  $\text{NO}_2^-$ , Fe, As,  $\text{Cr}^{6+}$ , and  $\text{NO}_2\text{-N}$  is more than 0.1, it can be considered that the concentration of these five parameters is the main influencing parameter of groundwater quality [41]. The calculation results of EWQI show that the EWQI is between 3.13 and 48.66, with an average value of 14.97, indicating that all the underground water quality in the study area is class 1 water. However, the EWQI value is the highest in the southwest of the study area, showing a trend of deterioration of groundwater water quality. As the assessment results of groundwater quality showed that the water quality was excellent, it was considered that the groundwater quality in the study area was very good, and the influence of natural filtration should be greater than that of human factors [42]. First of all, cation alternating adsorption leads to the gradual increase of Na concentration in the direction of groundwater flow in the study area. Secondly, the chemical components in groundwater are gradually formed and accumulated due to the combined influence of leaching and topography. A lesser man-made cause of the impact is presumed to be industrial enterprises in the area [43]. Through field investigation, it is found that there is an industrial concentration area in the southwest of the study area, which mainly produces leather products such as leather and bags. During the production process, wastewater containing pollutants will be produced, and some of the wastewater will be discharged into the

drainage ditch without treatment, which will pollute the water through infiltration.

For adults, 7.407% of the water sample sites were above the acceptable limit of noncarcinogenic risk, and for children, 55.556% of the water sample sites were in areas of noncarcinogenic risk. The major noncarcinogenic risk factors were  $F^-$ ,  $NO_2^-$ ,  $NO_3^-$ , and  $Cr^{6+}$ . The carcinogenic risk for adults ranged from 0 to  $6.91E 04$ , with a mean of  $1.00E 04$ . The carcinogenic risk for children ranged from 0 to  $1.03E 03$ , with a mean of  $1.55E 04$ . The carcinogenic risk is mainly due to the industrial production of As and  $Cr^{6+}$ . Therefore, it is necessary to take appropriate measures to reduce the levels of toxic parameters in groundwater, to reduce the carcinogenic and noncarcinogenic risks in groundwater.

Suggestions and measures for groundwater protection are put forward. These suggestions and measures include the treatment of possible industrial wastewater discharges in the tanneries and bag processing plants in the study area, cleaning up polluted rivers, strengthening the treatment and management of domestic sewage, and strengthening the related research in this field. This will help improve the groundwater situation in the study area and other similar areas.

## Data Availability

The basic data used to support the findings of this study were supplied by wangzhe under license and so cannot be made freely available. Requests for access to these data should be made to wangzhe, wangzhe0752@163.com.

## Conflicts of Interest

The authors declare that they have no competing interests.

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