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Using the Water Quality Index (WQI), and the Synthetic Pollution Index (SPI) to Evaluate the Groundwater Quality for Drinking Purpose in Hailun, China

(Penggunaan Indeks Kualiti Air (WQI) dan Indeks Pencemaran Sintetik (SPI) untuk Menilai Kualiti Air Bawah Tanah untuk Tujuan Minuman di Hailun, China)

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ABSTRACT

Due to the impact of human agricultural production, climate and environmental changes. The applicability of groundwater for drinking purposes has attracted widespread attention. In order to quantify the hydrochemical characteristics of groundwater in Hailun and evaluate its suitability for assessing water for drinking purposes, 77 shallow groundwater samples and 57 deep groundwater samples were collected and analyzed. The results show that deep groundwater in aquifers in the study area is weakly alkaline, while that in shallow is acidic. The abundance is in the order HCO, > $Cl > SO_4^{2-}$ for anions, and $Ca^{2+} > Na^{+} > Mg^{2+}$ for cations. Groundwater chemical type were dominated by HCO_3 -Ca, HCO₃-Ca• Mg, and HCO₃-Ca• Na. Correlation analysis (CA) and Durov diagram showed that rock weathering and dissolution, human activities, and the hydraulic connection between shallow and deep water are the main reasons affecting the chemical composition of water in Helen. The analysis of water samples based on the WQI model showed that about 23.37, 23.37, 32.46, 12.98, and 7.79% of the shallow groundwater samples were excellent, good, poor, very poor, and unsuitable for drinking purposes, respectively, and that 61.40, 30.90, 5.26, 1.75, and 1.75% of the deep groundwater samples were excellent, good, poor, very poor, and unsuitable for drinking purposes, respectively. The analysis of groundwater samples based on the SPI model showed that 92.98% of the deep groundwater samples were suitable grade, while that 40.25% of the shallow groundwater samples were suitable grade. The spatial distribution maps of the WQI and SPI show that most of the deep groundwater resources in the study area are clean and suitable for drinking, despite the risks of the shallow groundwater in the north and southwest of the study area.

Keywords: China; groundwater quality assessment; hydrochemistry; SPI; WQI

ABSTRAK

Kesan daripada pengeluaran pertanian manusia, iklim dan persekitaran mengalami perubahan. Kebolehgunaan air bawah tanah untuk tujuan minuman telah menarik perhatian meluas. Untuk mengukur ciri hidrokimia air bawah tanah di Hailun dan menilai kesesuaian air untuk tujuan minuman, 77 sampel air bawah tanah yang cetek dan 57 sampel air bawah tanah yang dalam telah diambil dan dianalisis. Keputusan menunjukkan bahawa air bawah tanah yang dalam di akuifer di kawasan kajian adalah alkali yang lemah, manakala di kawasan yang cetek adalah berasid. Kebanyakannya adalah dalam turutan $HCO_3^2 > Cl^2 > SO_4^2$ untuk anion, dan $Ca^{2+} > Na^+ > Mg^{2+}$ untuk kation. Jenis kimia air bawah tanah didominasi oleh HCO₃-Ca, HCO₃-Ca• Mg dan HCO₃-Ca• Na. Analisis korelasi (CA) dan rajah Durov menunjukkan bahawa luluhawa batuan dan pelarutan, aktiviti manusia, dan kaitan hidraulik antara air yang cetek dan dalam merupakan punca utama yang memberi kesan terhadap komposisi kimia air di Helen. Analisis sampel air berdasarkan model WQI menunjukkan bahawa 23.37, 23.37, 32.46, 12.98 dan 7.79% daripada sampel air bawah tanah yang cetek masing-masing adalah sangat baik, baik, tidak baik, sangat tidak baik, dan tidak sesuai untuk tujuan minuman dan 61.40, 30.90, 5.26, 1.75 dan 1.75% daripada sampel air bawah tanah yang dalam masing-masing adalah sangat baik, baik, tidak baik, sangat tidak baik, dan tidak sesuai untuk tujuan minuman. Analisis sampel air bawah tanah berdasarkan model SPI menunjukkan bahawa 92.98% daripada sampel air bawah tanah yang dalam merupakan gred yang sesuai. Peta taburan ruang untuk WQI dan SPI menunjukkan bahawa kebanyakan daripada sumber air bawah tanah yang dalam di kawasan kajian adalah bersih dan sesuai untuk diminum, walaupun terdapat risiko daripada air bawah tanah yang cetek di utara dan barat daya kawasan kajian.

Kata kunci: China; hidrokimia; penilaian kualiti air bawah tanah; SPI; WQI

INTRODUCTION

Water is one of the natural resources necessary for human survival and economic development (Boyd et al. 2019). However, in arid and semi-arid regions, uneven distribution of groundwater and surface water resources has become a contradiction that restricts living standards and economic development (Brhane et al. 2018). Understanding the relationship between groundwater and water demand for agricultural production is important for sustainable agricultural development (Zanotti et al. 2019). Groundwater has become the main source of fresh water for household, agricultural, and industrial uses due to its simple extraction and low cost (Hasan et al. 2017). In agricultural production areas, irrigation water, surface water and groundwater are closely linked, which has changed the hydrodynamic conditions and led to changes in groundwater hydrochemical conditions (Li et al. 2019).

Therefore, understanding the chemical characteristics of groundwater and its influencing factors are critical to the protection and management of groundwater resources and the sustainable use of groundwater (Madlala et al. 2019). The Songnen Plain is one of the most important grain and grass production bases in China (Chen et al. 2019). Hailun is an important part of the northeast of the Songnen Plain and plays an important role in agricultural production. After 1995, grain production increased significantly, especially rice production. At the same time, with the increase of rice yield, groundwater irrigated area increased rapidly (Chen et al. 2019). The contradiction between the uneven distribution of water resources and the demand for irrigation water has become increasingly prominent, and farmers have to extract groundwater from aquifers for dryland irrigation. In the end, it will lead to a series of environmental geological problems, such as soil secondary salinization (Zhao et al. 2019), the core of depression (Sun et al. 2019; Zhao et al. 2010), wetland degradation (Li et al. 2019; Wu et al. 2019), and water quality deterioration (Tian et al. 2020a, 2019). However, the hydrogeochemical characteristics and drinking water quality of groundwater in agricultural irrigation areas (Hailun) are still not particularly clear. This may restrict the protection and proper use of groundwater resources, especially the drinking water safety issues of local residents.

In order to study the hydrochemical status and the quality of groundwater in Hailun, and quantitatively analyze the applicability of groundwater for drinking, 77 shallow groundwater samples and 57 deep groundwater samples were collected from Hailun between June and October in 2019. Using GIS and SPSS software, the hydrochemical properties and evolution of groundwater in the study area were characterized. The special purpose of this study was to: explore the hydrochemical characteristics of groundwater; understand the evolution of groundwater through Factor Analysis, and PCA analysis;

and assess the applicability of groundwater as drinking water according to the parameters recommended in the WHO guidelines and using WQI and SPI models.

The results of the study help local governments strengthen management and governance in places where the groundwater environment is fragile, thereby effectively using groundwater resources in the river basin.

STUDY AREA

STUDY AREA DESCRIPTION

Helun is located in the middle of Heilongjiang Province in northeast China, adjacent to the northeast edge of the Songnen Plain. The study area is between 46° 58 'and 47° 52' N, and 126° 14 'and 127° 45' E, with an area of 4668 km². The area is located in the mid-latitudes of the northern hemisphere and is a temperate continental semi-humid monsoon climate with four distinct seasons. The study area includes the urban area of Helen and 23 townships (Figure 1(b)). The total population of the study area is approximately 799,838. The annual average temperature is 1-2 °C, and the precipitation is between 550 and 600 mm, which is mostly concentrated in June-August. The annual average evaporation is 1374 mm, and the altitude of the study area is 190-400 m (Xing et al. 2019). The terrain slopes from southeast to the northwest. The study area contains four types of landforms: The hilly area in the northeast, the high plains in the east, the sloping plains in the middle, and the terraces and floodplains in the west (Li et al. 2019). The Hailun, Zhayin, and Sandaowulong Rivers flow through the area, indicating that surface water resources are abundant. The surface water is mainly used for farmland irrigation, especially rice farming. In the dry period, when the river water is dry and cannot meet the needs of agricultural production, large areas of groundwater are often extracted for irrigation.

GEOLOGY AND HYDRO-GEOLOGY

Under the control of neotectonic movements and geomorphological conditions, the Quaternary strata of the study area formed obvious differences between the northeast hilly areas, the eastern high plains, and the western plains (Figure 1(a)).

In the hilly area in the northeast, its internal structure has many sedimentary features, mainly Quaternary flood and alluvial layers. Its lithology is mainly silty clay which contains gravel locally and has a thickness of less than 5 m. The Cretaceous Nenjiang Formation is below the Quaternary strata, and its lithology is siltstone, fine sandstone and shale, which are the main aquifers in this area. The aquifer is very thick and multi-layered, which is the main feature of this area. The groundwater level is buried at a depth of 5-15 m. The output of the Cretaceous confined aquifer is generally less than 300 tons/day (Tian et al. 2020b).

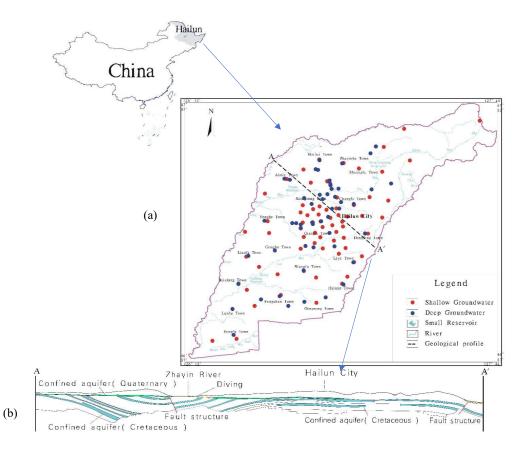


FIGURE 1. (a) Location and sampling sites of the study area and, (b) hydrogeological profile

In the eastern high plains, quaternary alluvial, flooding and lacustrine strata are widely distributed. The upper part is alluvial and lacustrine sedimentary strata. The lithology is mainly subclay, with vertical joints, but the porosity is small. The lower part is a lacustrine sedimentary stratum, with lithology of light yellow subclay, containing a large amount of iron-manganese nodules and humus, and the layer thickness is 15.0-36.0 m. In this area, only Cretaceous confined water aquifers are developed, and the water output of aquifers is generally less than 100 tons/day (Niu et al. 2019).

In the western plains, Neogene alluvial, marsh sediments and Pleistocene alluvial are widely distributed. Quaternary strata are 7.8-30 m thick. The upper part of the formation is brownish yellow and yellow silty clay, and the lower part is gray-black muddy subclay. Cretaceous formations are mudstone and sandstone. The lithology of the aquifer is fine sand, gravel, sandstone, and fine sandstone. Quaternary diving, confined water and Cretaceous confined water, are the main mining layer in the area (Zhang et al. 2012). Under normal circumstances, the water output of a single well is 300-500 tons/day.

MATERIALS AND METHODS

SAMPLING AND MEASUREMENTS

According to the research plan, a total of 77 samples of shallow groundwater samples and 57 samples of deep groundwater samples were collected in two batches from June to October 2019. Deep groundwater samples were taken from the water supply wells in each town, and the depth was greater than 90 meters, which was confined water of the Cretaceous Nenjiang Formation. Shallow groundwater samples are taken from wells that are mainly used for water supply and irrigation in rural areas. Generally, the depth of the well is less than 40 m, and its distribution is shown in Figure 1(a). The spatial distribution of sampling points is consistent with the distribution of water wells in each village, which can objectively reflect the characteristics of groundwater extraction in the study area. During the sampling process, each sampling well must be cleaned in accordance with the groundwater sampling guidelines, and the pumping time is greater than 10 min. In the sampling process, the first step was to rinse the vial with well water three times, then filled with water and sealed. In the second step, the groundwater sample was stored in a 4 °C incubator. The third step was to return the sample to a qualified laboratory for testing. After the sampling was completed, groundwater samples were tested in the laboratory of the Shenyang Institute of Geology and Mineral Resources within three days.

The laboratory test index includes TDS, TH, Ca, Mg, K, Na, Cl, SO₄, HCO₃, NO₃, NO₂, Fe, Mn, Cr, and Pb. TDS and Ph were measured in the field using a calibrated multi-parameter water quality analyzer (HACH-HQ40D). The concentration of NO₂ and NH₄ were obtained using gas phase molecular absorption spectrometry (GMA-3376). The concentrations of major anions (Cl, SO₄, and NO₃) were determined in the laboratory using ion chromatography (ICS-3000) and the concentration of major cations (Ca, Na, K, and Mg) was determined in the laboratory using plasma spectroscopy (ICP-6300).

PRINCIPAL COMPONENT ANALYSES (PCA) AND CA

PCA aims to use the idea of dimensionality reduction to transform multiple indicators into a few comprehensive indicators, where each principal component can reflect most of the information of the groundwater. The main steps in applying factor analysis are as follows: standardize the data samples, calculate the correlation matrix R of the samples, calculate the eigenvalue and eigenvectors of the correlation matrix R. Select variables with eigenvalues greater than 1, (4) determine the number of main factors according to the cumulative contribution rate required by the system. The cumulative contribution rate is chosen to be greater than 80%, (5) calculate the loaded factor matrix A, (6) establish a factor model, and (7) based on

the calculation results, analyze the relationship of factors in groundwater.

CA is one of the common methods used to evaluate the relationship between two variables. Using the established correlation coefficient matrix between variables, the potential connections between variables can been analyzed. If 0 < R < 1, it means that the two variables are positively correlated in linear. If -1 < R < 0, it means that the two variables are negatively correlated in linear. In special cases, if R = 0, it means that there is no relationship between the two variables.

DRINKING WQI

WQI is a simple and useful approach for determining the overall quality of groundwater and its suitability for drinking purposes, and it has been widely used over the world (Wagh et al. 2019). The WQI was originally invented by Brown in 1970, and then improved by Backman in 1998. The World Health Organization (WHO) report (WHO 2008) emphasized that the WQI model helps to identify the impact of individual parameters of water quality and their combination on drinking water quality. Therefore, the WQI model can be used as a reliable tool for groundwater quality assessment (Sener et al. 2017). Specifically, the WQI model can be divided into four steps, including relative weight (W_i) calculation, the quality rating (q_i) calculation, the subindex of parameter (SI_i), and the result of WQI.

Step 1: The relative weight (W_i)

$$W_{i} = \sum \frac{W_{i}}{\sum_{i=1}^{n} W_{i}}$$
(1)

where W_i is the relative weight of each parameter; and *n* refers to the number of parameters. The weight (w_i) and relative weight (Wi) of each chemical parameter are shown in Table 1. As shown in Table 1, the weight (w_i) and relative weight (Wi) of each parameter are according to WHO standards (Soleimani et al. 2018).

Parameters	Units	Weight (w_i)	Relative weight (Wi)	Limit values	References
TDS	mg/L	4	0.063	500	(WHO 2018)
TH	mg/L	4	0.063	500	(WHO 2018)
PH	-	2	0.032	6.5-8.5	(WHO 2018)
COD	mg/L	5	0.079	10	(WHO 2018)
Na	mg/L	4	0.063	200	(WHO 2018)
Са	mg/L	3	0.048	300	(WHO 2018)
Mg	mg/L	3	0.048	30	(WHO 2018)
HCO ₃	mg/L	1	0.016	120	(WHO 2018)
Cl	mg/L	4	0.063	250	(WHO 2018)

TABLE 1. The weight (w_i) and relative weight (W_i) of each chemical parameter

SO_4	mg/L	3	0.048	250	(WHO 2018)
NO ₃	mg/L	5	0.079	50	(WHO 2018)
NO ₂	mg/L	5	0.079	3	(WHO 2018)
Fe	mg/L	5	0.079	1	(Wooding et al. 2017)
Mn	mg/L	5	0.079	0.3	(Sener et al. 2017)
Pb	mg/L	5	0.079	0.01	(WHO 2018)
Cr	mg/L	5	0.079	0.05	(WHO 2018)
SUM	-	$\sum W_i = 63$	$\sum w_i = 1$	-	

Step 2: The quality rating scale is the concentration of ions in the groundwater sample divided by the respective standard (WHO 2008 version) and multiplied by 100.

$$q_i = \left(\frac{c_i}{s_i}\right) \times 100 \tag{2}$$

where C_i is the concentration (mg/L) of ion chemical parameters in the sample; and S_i is the limit value (mg/L) of the corresponding chemical parameter in the guidelines issued by the World Health Organization (2008).

Step 3: The subindex of parameter (SI.)

$$SI_i = W_i \times q_i \tag{3}$$

where qi represents the rating based on concentration of its parameter; Wi is the relative weight, SI_i is the subindex of parameter (Kumar et al. 2017).

Step 4: The result of WQI for a single water sample

$$WQI = \sum_{i=1}^{n} SI_i \tag{4}$$

where n is the number of parameters. According to WQI classification standards, water quality can be divided into five categories, as shown in Table 2.

TABLE 2. Water quality classification based on WQI classification standards (Khan & Jhariya 2017)

Range (WQI)	Type of groundwater
<50	Excellent water
50≤WQI<100	Good water
100≤WQI<200	Poor Water
200≤WQI<300	Very poor water
≥300	Unsuitable for drinking/Irrigation purpose

THE SPI

The SPI model can be divided into three steps, including the constant of proportionality (K_i) , the weight coefficient (W_i) , and SPI. The derivation and calculation of SPI involves the following three steps (Solangi et al. 2018):

Step 1: The proportionality (K_i)

$$K_i = \frac{1}{\sum_{i=1}^n \frac{1}{S_i}} \tag{5}$$

Step2: The weight coefficient (W_i)

$$W_i = \frac{K_i}{S_i} \tag{6}$$

Step 3: The SPI

$$SPI = \sum_{i=1}^{n} \frac{c_i}{s_i} \times Wi \tag{7}$$

In equations (5), (6), and (7), n is the number of water quality parameters for analysis, and Si is the threshold value of each parameter according to the WHO guidelines. According to SPI classification standards, water quality can be divided into five categories, as shown in Table 3.

TABLE 3. Water quality classification based on SPI classification standards (Gautam et al. 2015)

Range (SPI)	Type of groundwater
SPI<0.2	suitable
0.2≤SPI<0.5	slightly polluted
0.5≤SPI<1.0	moderately polluted
1.0≤SPI<3.0	highly polluted
SPI≥3.0	unsuitable for drinking purposes

SOFTWARE

This article uses SPSS statistical analysis software and GIS software. MapGIS6.7 software is the basic software platform for geographic information systems independently developed by China. MAPGIS6.7 is used to draw the location map of the study area, the distribution map of sampling points, the water chemistry type map, WQI and SPI evaluation map. SPSS19.0 is used for analysis and statistics of the component of anions and cations in water, and for principal component analysis.

RESULTS AND DISCUSSION

The groundwater chemistry is mainly affected by both natural and human factors. Natural factors include regional geological conditions, chemical composition of precipitation, hydrogeological conditions, and water-rock interactions (oxidation, reduction). Human factors include pesticide use, fertilizer use, groundwater extraction, groundwater recharge, and biological and microbial effects.

PHYSICOCHEMICAL CHARACTERISTICS

The results of statistical analysis of physical and chemical indicators of all groundwater samples are shown in Table 4. TDS and TH of groundwater in the shallow aquifer are observed in the ranges of 98.91-1920.13 and 60.27-1020.71 mg/L, respectively, and those in the deep aquifer are 39.78-421.05 and 95.29-826.57 mg/L, respectively. According to WHO guidelines, the TDS and TH allowable value for drinking water is less than 500 mg/L. The pH range of groundwater observed in shallow aquifers is 6.14-7.60, and the pH range observed in deep aquifers is 6.40 to 8.07, which indicates that the shallow groundwater in the study area is weakly acidic, while the deep groundwater is weakly alkaline. According to WHO guidelines, the safe range of pH value for drinking water is 6.5-8.5. The COD in the water represents the degree of pollution of the water environment. The value of the COD for the shallow groundwater in the study area is 0.11-23.73 mg/L, and for the deep groundwater in the study area is 0.43-3.88 mg/L. Anions and cations show significant difference in deep and shallow groundwater. As shown in Table 4, the concentrations of SO₄²⁻, HCO₃⁻, and Cl⁻ in deep groundwater are observed in the ranges of 0.13-72.24, 25.75-660.80, and 0.31-147.00 mg/L, respectively, and those in shallow groundwater are in the ranges of 0.21-448.97, 34.67-809.00, and 0.13-317.38 mg/L, respectively. Both in shallow and deep groundwater, the average concentration of anions analyzed is in the order of $HCO_3^- > Cl^- > SO_4^{-2}$. The concentrations of Ca2+, Mg2+, and Na+ in deep groundwater are observed in the ranges of 10.94–110.10, 2.03-35.09, and 3.57-206.00 mg/L, respectively. While in shallow groundwater, the concentrations are observed in the ranges

of 16.12-315.00, 3.75-70.37, and 4.90-215.97 mg/L, respectively. For both shallow and deep groundwater, the abundance of cations is in the following order: $Ca^{2+} > Na^+ > Mg^{2+}$. It is worth noting that the concentrations of anions and cations in shallow groundwater are higher than those in deep groundwater.

According to studies, nitrate nitrogen in water has a greater harmful effect on humans and aquatic organisms. For example, when water with a nitrate content of greater than 10 mg/L is consumed over time, methemoglobinemia occurs. A blood methemoglobin content of 70 mg/L results in suffocation. In this study, the concentration of NO₃ in shallow groundwater are in the range of 0.00 - 497.84 mg/L with the mean value of 63.40 mg/L (Figure 2(a)).

The concentration of NO₃ in deep groundwater are in the range of 0.02 - 139.43 mg/L with the mean value of 9.81 mg/L (Figure 2(b)). The concentration of NO₂ in shallow groundwater are in the range of 0.00 - 7.32mg/L with the mean value of 0.28 mg/L (Figure 2(c)). The concentration of NO₂ in groundwater are in the range of 0.00 - 4.85 mg/L with the mean value of 0.23 mg/L (Figure 2(d)). According to WHO guidelines, the allowable concentration for NO₂ is 3 mg/L. The increase of nitrate concentration is closely related to the use of chemical fertilizers and the infiltration of surface nitrogen (van Dijk et al. 2019).

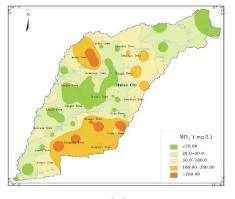
In recent years, the concentrations of Fe and Mn in groundwater have received much attention and have been included in the evaluation standards for drinking water. In this study, Fe and Mn of groundwater in the shallow aquifer are observed in the ranges of 0.07-497.89 mg/L and 0.003-15.70 mg/L (Figure 2(e) and 2(g)), respectively, and those in the deep aquifer are 0.06-39.33 mg/L and 0.001-1.93 mg/L (Figure 2(f) and 2(h)), respectively. According to WHO guidelines, the allowable concentration for Fe in water is 1 mg/L, and the limited concentration for Mn is 0.3 mg/L. The high concentrations of Fe and Mn in groundwater indicate high concentrations of Fe and Mn in depositional environment in the aquifer throughout the study area (Rotiroti et al. 2013).

High levels of heavy metals in drinking water can cause poisoning, carcinogenesis and various diseases (Ravindra et al. 2019). In this study, Cr and Pb of groundwater in the shallow aquifer are observed in the ranges of 0.0007-0.0094 and 0.00-0.0838 mg/L (Figure 2(i) and 2(l)), respectively, and those in the deep aquifer are 0.00-0.0046 and 0.00-0.0013 mg/L (Figure 2(j) and 2(m)), respectively. According to WHO guidelines, the allowable concentration for Cr in water is 0.01 mg/L, and the limited concentration of Cr and Pb is within the limited range, which indicates that the content of heavy metals in groundwater is low.

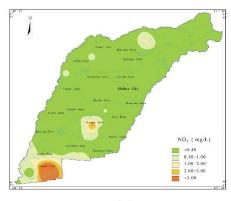
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	Parameters	Unit	Minimum	Maximum	Mean	SD	CV(%)
	TH	mg/L	60.27	1020.71	373.23	229.84	61.58
	TDS	mg/L	98.91	1920.13	561.81	396.26	70.53
	pН	-	6.14	7.60	6.93	0.35	5.07
	COD	mg/L	0.11	23.73	3.11	3.74	120.21
	Ca	mg/L	16.12	315.00	106.01	70.65	66.64
	Mg	mg/L	3.75	70.37	23.72	14.15	59.65
~	Na	mg/L	4.90	215.97	35.23	37.26	105.75
Shallow GW	Cl	mg/L	0.13	317.38	87.01	89.58	102.95
allov	SO_4	mg/L	0.21	448.97	62.97	80.78	128.29
Sh	HCO ₃	mg/L	34.67	809.00	249.79	126.41	50.61
	NO3	mg/L	0.0000	497.84	63.40	107.42	169.43
	NO ₂	mg/L	0.0000	7.32	0.28	0.91	324.28
	Fe	mg/L	0.0706	497.89	56.67	108.93	192.21
	Mn	mg/L	0.0038	15.70	1.33	2.04	153.70
	Cr	mg/L	0.0007	0.00940	0.00364	0.00205	56.36
	Pb	mg/L	0.0000	0.08388	0.00175	0.00959	548.54
	TH	mg/L	95.29	826.57	332.05	123.99	37.34
	TDS	mg/L	39.78	421.05	200.23	80.90	40.40
	pН	-	6.40	8.07	7.50	0.35	4.71
	COD	mg/L	0.43	3.88	1.50	0.71	47.41
	Ca	mg/L	10.94	110.10	52.69	22.00	41.75
	Mg	mg/L	2.03	35.09	15.01	7.54	50.23
	Na	mg/L	3.57	206.00	42.80	42.06	98.26
GW	Cl	mg/L	0.31	147.00	20.77	28.28	136.14
Deep GW	SO_4	mg/L	0.13	72.24	13.66	14.29	104.58
Ι	HCO ₃	mg/L	25.75	660.80	284.78	112.22	39.40
	NO ₃	mg/L	0.0246	139.43	9.81	23.05	234.92
	NO ₂	mg/L	0.0000	4.85	0.23	0.70	311.03
	Fe	mg/L	0.0640	39.33	2.54	6.83	268.93
	Mn	mg/L	0.0018	1.93	0.45	0.48	105.93
	Cr	mg/L	0.0000	0.0046	0.0006	0.0011	179.50
	Pb	mg/L	0.0000	0.0013	0.0002	0.0003	136.22

TABLE 4. Statistics of the measured parameters for groundwater samples

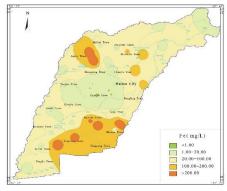
CV=Coefficient of variation, SD= Standard deviation



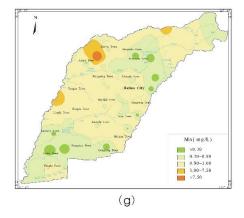


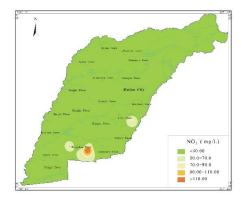




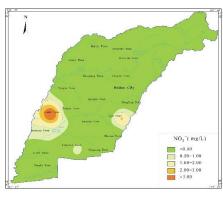




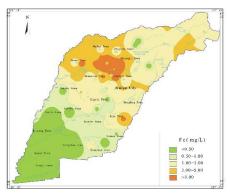




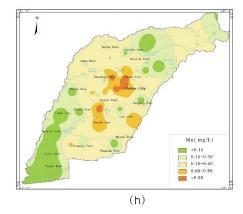




(d)







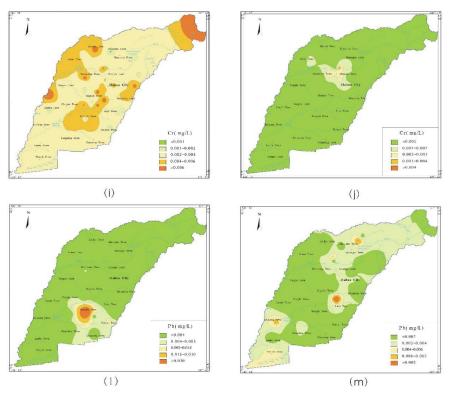


FIGURE 2. (a) concentration of NO₃ in shallow groundwater, (b) concentration of NO₃ in deep groundwater, (c) concentration of NO₂ in shallow groundwater, (d) concentration of NO₂ in groundwater, (e) concentration of Fe in groundwater in the shallow aquifer, (f) concentration of Fe in the deep aquifer, (g) concentration of Mn in groundwater in the shallow aquifer, (h) concentration of Mn in the deep aquifer, (i) concentration of Cr of groundwater in the shallow aquifer, (j) concentration of Cr in the deep aquifer, (l) concentration of Pb of groundwater in the shallow aquifer concentration of Cr and Pb of groundwater in the shallow aquifer of Pb in the deep aquifer

THE DUROV DIAGRAM AND GROUNDWATER HYDROCHEMICAL TYPES

In order to accurately reflect and describe the groundwater chemistry in the study area, the Durov chart was drawn using MapGIS 6.7 software (Karunanidhi et al. 2020). As shown in Figure 3, chemical differences between shallow groundwater and deep groundwater are also reflected. The shallow groundwater samples had a larger variated range of TDS content varying from 100-1900 mg/L, while the TDS of deep groundwater are less than 550 mg/L. The

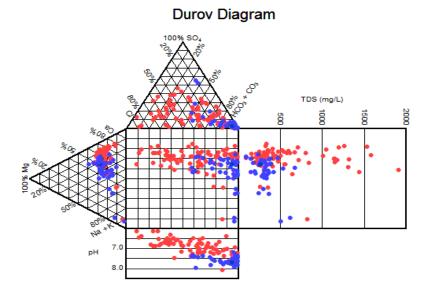


FIGURE 3. Durov diagram of groundwater samples (red-shallow GW; blue-deep GW)

diagram also shows that Ca and Na are the main cations in groundwater, and HCO_3 and Cl are the main anions. The concentration of Na ion is closely related to evaporation and ion exchange of diving. According to the Durov chart, the groundwater in the deep and shallow aquifers in the Helen area is mainly controlled by HCO_3 -Ca, HCO_3 -Ca• Mg, and HCO_3 -Ca• Na types.

PCA AND CA

PCA and CA can help identify relationships and sources of ions in groundwater. Three principal components

with characteristic root values greater than 1 in shallow groundwater were extracted and analyzed (Figure 4(a), Table 5). Factor 1, with a variance of about 47.93%, includes TDS, TH, Na⁺, Ca²⁺, Mg²⁺, SO₄²⁻, and Cl⁻, suggesting that TDS and TH content of shallow groundwater are mainly affected by Ca²⁺ and Mg²⁺ in the study area (Ravikumar & Somashekar 2017). The high correlation between Ca²⁺, Mg²⁺ and Na⁺ indicates that a strong exchange adsorption occurs between Ca²⁺, Mg²⁺ and Na⁺ in groundwater. Factor 2 controls 17.28% of the shallow groundwater chemistry parameters, including pH, and HCO₃⁻. The high correlation

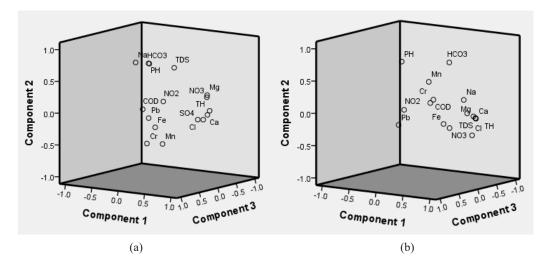


FIGURE 4. PCA plot of the (a) deep, and (b) shallow groundwater

between HCO_3^- , and pH indicates that shallow groundwater is weakly acidic and is mainly caused by bicarbonate. Factor 3 contains 16.89% of all variables, including NO_2^- and P_b^- , suggesting the amount of NO_2^- in groundwater is highly correlated with the content of Pb (Dippong et al. 2019). The high levels of NO_2^- and P_b^- are closely related to human activities, especially the use of chemical fertilizers, domestic sewage irrigation, and landfill leakage. Factors 3 also suggest that shallow groundwater in some areas has been contaminated with agricultural chemical fertilizers, indicating that groundwater recharged by agricultural irrigation water is the main cause of groundwater pollution (Abbasnia et al. 2018).

Similarly, three main components with characteristic root values greater than 1 in deep groundwater were extracted and analyzed (Figure 4(b), Table 5). Factor 1, with a variance of about 35.96%, includes TDS, TH, Ca^{2+} , Mg^{2+} , NO_3^{-} , and Cl⁻, suggesting that TDS and TH content

of groundwater are mainly affected by Ca²⁺ and Mg²⁺ ions in the study area, and that is consistent with shallow groundwater. The high correlation between Cl⁻, and NO₂⁻ indicates that their sources are consistent and are closely related to the use of fertilizers. It proves that agricultural production activities have an impact on shallow and deep groundwater, and also shows that there is a close hydraulic connection between shallow groundwater and deep groundwater (Misaghi et al. 2017). Factor 2 controls 27.57% of the water chemistry parameters, including Na⁺, and HCO₃. The high correlation between HCO₃, and Na⁺ indicates that their sources are consistent and are closely related to the rock weathering and dissolution (Gastmans et al. 2017). Factor 3 contains 18.16% of all variables (including Cr and Mn), indicating that the content of Cr in groundwater is consistent with the content of Mn, both of which come from the dissolution of Mn and Cr in water in the aquifer (Hausladen et al. 2018).

	TDS	TH	PH	COD	Ca	Mg	Na	Cl	SO_4	HCO_3	NO_3	NO_2	Fe Mn	Cr	Pb		
	TDS	1.00															
	TH	0.98	1.00														
	pН	-0.30	-0.31	1.00													
	COD	0.51	0.45	-0.06	1.00												
	Ca	0.97	0.99	-0.28	0.39	1.00											
	Mg	0.91	0.93	-0.34	0.52	0.88	1.00										
	Na	0.78	0.69	-0.06	0.52	0.69	0.65	1.00									
, GW	Cl	0.83	0.84	-0.51	0.26	0.83	0.83	0.58	1.00								
Shallow GW	SO_4	0.89	0.82	-0.22	0.55	0.83	0.71	0.83	0.67	1.00							
S	HCO_3	0.40	0.42	0.30	0.24	0.41	0.41	0.53	0.10	0.39	1.00						
	NO ₃	0.75	0.67	-0.25	0.64	0.65	0.68	0.60	0.54	0.64	0.08	1.00					
	NO ₂	0.09	0.16	-0.06	0.23	0.14	0.05	0.05	0.02	0.08	0.10	0.10	1.00				
	Fe	0.65	0.57	-0.20	0.65	0.55	0.59	0.60	0.46	0.58	0.10	0.98	0.12	1.00			
	Mn	0.20	0.20	-0.03	0.49	0.13	0.32	0.15	0.17	0.12	0.33	0.15	0.09	0.16	1.00		
	Cr	0.11	0.12	0.01	-0.03	0.12	0.10	0.12	0.14	0.05	0.05	0.02	0.05	-0.01	0.13	1.00	
	Pb	0.07	0.06	-0.10	0.18	0.04	0.02	0.10	-0.02	0.14	-0.08	0.15	0.37	0.16	-0.04	0.00	1.00
	TDS	1.00															
	TH	0.34	1.00														
	pН	0.10	-0.27	1.00													
	COD	0.14	0.11	-0.14	1.00												
	Ca	0.30	0.94	-0.28	0.05	1.00											
	Mg	0.41	0.88	-0.08	0.12	0.73	1.00										
	Na	0.72	-0.33	0.35	0.16	-0.36	-0.15	1.00									
M	Cl	0.45	0.45	-0.45	-0.13	0.43	0.40	0.01	1.00								
Deep GW	SO ₄	0.15	0.45	-0.24	-0.15	0.45	0.40	-0.19	0.50	1.00							
Д	HCO ₃	0.70	0.23	0.30	0.24	0.18	0.32	0.64	-0.15	-0.30	1.00						
	-											1.00					
	NO ₃	0.42	0.43	-0.10	-0.17	0.40	0.45	0.06	0.50	0.53	-0.09	1.00					
	NO ₂	0.07	0.02	0.01	0.21	0.03	-0.01	0.07	0.00	-0.04	-0.03	0.23	1.00				
	Fe	-0.12	0.07	-0.22	0.08	-0.13	-0.05	-0.13	0.01	-0.04	-0.13	-0.08	0.01	1.00			
	Mn	0.03	0.33	-0.59	0.27	0.35	0.16	-0.21	0.34	-0.01	-0.04	-0.01	-0.07	0.09	1.00		
	Cr	0.10	0.05	-0.63	0.27	0.16	-0.17	-0.05	0.26	0.08	-0.04	-0.14	-0.09	0.01	0.54	1.00	
	Pb	0.01	-0.07	-0.11	-0.23	0.01	-0.17	0.04	0.03	-0.13	0.01	-0.08	-0.08	-0.07	0.05	0.19	1.00

TABLE 5. Groundwater physical and chemical parameter correlation matrix

WATER QUALITY FOR DRINKING PURPOSE

The results of groundwater WQI in Hailun area are shown in Figure 5 (Tables 6 & 8). As shown in Figure 5, among the 77 shallow groundwater samples, 18 were 'excellent' (grade 1), 18 were 'good' (grade 2), 25 was 'poor' (grade 3), 10 were 'very poor' (grade 4), and 6 were 'unsuitable' (grade 5), accounting for 23.37, 23.37, 32.46, 12.98, and 7.79%, respectively. Similarly, for 57 deep groundwater samples, 35 were 'excellent' (grade 1), 17 were 'good' (grade 2), 3 was 'poor' (grade 3), 1 was 'very poor' (grade 4), and 1 was 'unsuitable' (grade 5), accounting for 61.40, 30.90, 5.26, 1.75, and

1.75%, respectively. The quality of deep groundwater is significantly better than that of shallow groundwater. The calculation results of WQI show that the deep groundwater

in the study area is excellent for drinking purpose, while the shallow groundwater in some places is not suitable for drinking (Solangi et al. 2019).

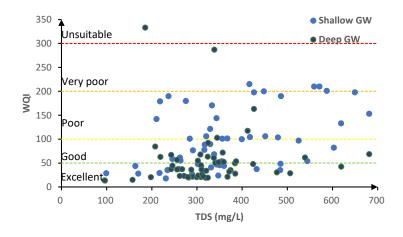


FIGURE 5. The diagram of Groundwater TDS versus WQI

The results of groundwater SPI in Hailun area are shown in Figure 6 (Tables 7 & 9). As shown in Figure 6, among the 77 groundwater samples, 31 were 'suitable' (grade 1), 24 were 'slightly polluted' (grade 2), 6 were 'moderately polluted' (grade 3), 12 were 'highly polluted' (grade 4), and 4 were 'unsuitable' (grade 5), accounting for 40.25, 31.16, 7.79, 15.58, and 5.19%, respectively. Similarly, for 57 deep groundwater samples, 53 were 'suitable' (grade 1), and 4 were 'slightly polluted' (grade 2), accounting for 92.98, and 7.02%, respectively. The calculation results of SPI show that the deep groundwater in the study area is suitable for drinking, while the shallow groundwater in some places is unsuitable (Eslami et al. 2017).

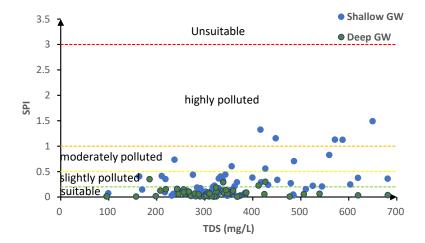


FIGURE 6. The diagram of Groundwater TDS versus SPI

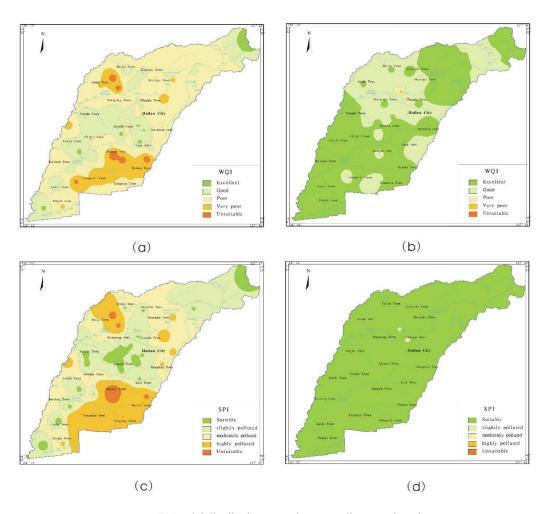


FIGURE 7. Spatial distribution groundwater quality maps based on the outcomes of the WQI model and SPI model

Based on the evaluation results of the water quality index model, the drinking water quality evaluation map of the study area was drawn (Figure 7). The spatial distribution of the water quality index shows that most of the deep groundwater index concentration ranges in the study area are below the WHO guidelines and are therefore suitable for drinking (Figure 7(b)). It is worth noting that in the southwest of the study area, the WQI index of shallow groundwater in small areas was found to be higher than 200 (Figure 7(a)). The WQI index exceeded the standard, mainly due to the extremely high concentration of Fe and Mn in groundwater. The high concentrations of Fe and Mn are not only affected by high concentrations in the Cretaceous aquifer, but also affected by human agricultural production (Adhikary et al. 2011). Therefore, the centralized water supply wells in this area should be added with Fe and Mn purification devices before

drinking. Overall, it was learned from this study that the quality of groundwater complies with drinking water specifications according to WHO guidelines.

Based on the evaluation results of the SPI model, the drinking water quality evaluation map of the study area was drawn (Figure 7). The spatial distribution of the SPI shows that the deep groundwater indicators in most areas of the study area do not exceed the WHO guidelines, but there are signs of shallow groundwater pollution in some places (Figure 7(d)). Similar to the WQI spatial distribution results, in the north and southwest of the study area, the SPI index of shallow groundwater in small areas was found to be higher than 1.00. The SPI index exceeds 1.0, indicating that there is a high risk of contamination of groundwater in these areas, mainly due to the extremely high content of Pb in groundwater. The high concentration of Pb is mainly due to the impact of human activities (Dong et al. 2009). In this area, there are small-scale landfills, and the leakage of landfill leachate contaminates shallow groundwater, leading to an increase in Pb concentration. Therefore, in order to prevent serious pollution of groundwater, the leakproof layer of the landfill should be reinforced.

THE RELATIONSHIP BETWEEN WQI AND SPI MODELS

The relationship between the WQI and SPI models is established, and the water categories indicated by the two models are correlated through regression analysis, Equations (8) and (9). The relationship indicates a good correlation between WQI and SPI models ($R^2 = 0.701$, $R^2 = 0.7322$).

$$SPI_{Shallow} = 0.0111 \times WQI_{Shallow} - 0.7223$$
(8)

$$SPI_{Deep} = 0.0012 \times WQI_{Deep} + 0.0173$$
(9)

The WQI and SPI models provide efficient methods for valuable information about the overall quality of shallow groundwater and deep groundwater. Therefore, according to this study, it can be concluded that proper treatment of shallow groundwater in the study area is vital to the health of residents in the area.

NO.	WQI	Rank	NO.	WQI	Rank	NO.	WQI	Rank
1	37.50	Excellent	27	101.07	Poor	53	43.44	Excellent
2	54.13	Good	28	96.62	Good	54	206.00	Very poor
3	29.21	Excellent	29	35.42	Excellent	55	48.48	Excellent
4	133.66	Poor	30	53.85	Good	56	325.00	Unsuitable
5	82.16	Good	31	180.00	Poor	57	44.07	Excellent
6	27.07	Excellent	32	61.57	Good	58	68.54	Good
7	101.41	Poor	33	198.00	Poor	59	144.00	Poor
8	85.22	Good	34	100.00	Poor	60	35.33	Excellent
9	97.03	Good	35	170.72	Poor	61	47.07	Excellent
10	198.00	Poor	36	28.73	Excellent	62	387.00	Unsuitable
11	133.00	Poor	37	89.60	Good	63	210.00	Very poor
12	41.00	Excellent	38	210.00	Very poor	64	106.09	Poor
13	103.75	Poor	39	190.00	Poor	65	398.00	Unsuitable
14	62.90	Good	40	250.00	Very poor	66	198.00	Poor
15	121.38	Poor	41	190.00	Poor	67	255.00	Very poor
16	77.84	Good	42	200.00	Very poor	68	245.00	Very poor
17	105.92	Poor	43	180.00	Poor	69	47.85	Excellent
18	104.44	Poor	44	201.00	Very poor	70	399.00	Unsuitable
19	17.87	Excellent	45	142.00	Poor	71	345.00	Unsuitable
20	153.04	Poor	46	389.00	Unsuitable	72	58.88	Good
21	24.04	Excellent	47	215.00	Very poor	73	49.01	Excellent
22	100.99	Poor	48	58.55	Good	74	240.00	Very poor
23	123.26	Poor	49	55.33	Good	75	145.27	Poor
24	76.75	Good	50	43.94	Excellent	76	63.51	Good
25	45.59	Excellent	51	179.00	Poor	77	70.88	Good
26	88.53	Good	52	27.90	Excellent			

TABLE 6. Categories of shallow groundwater based on the WQI model results

NO.	SPI	Rank	NO.	SPI	Rank	NO.	SPI	Rank
1	0.24	SP*	27	0.61	MP*	53	0.06	S*
2	0.21	SP*	28	0.14	S*	54	1.02	HP*
3	0.09	S*	29	0.05	S*	55	0.03	S*
4	0.29	SP*	30	0.14	S*	56	2.55	HP*
5	0.25	SP*	31	0.44	SP*	57	0.06	S*
6	0.10	S*	32	0.12	S*	58	0.33	SP*
7	0.29	SP*	33	0.95	MP*	59	0.44	SP*
8	0.09	S*	34	0.38	SP*	60	0.06	S*
9	0.22	SP*	35	0.40	SP*	61	0.08	S*
10	0.56	MP*	36	0.08	S*	62	4.24	U*
11	0.38	SP*	37	0.17	S*	63	0.83	MP*
12	0.09	S*	38	1.13	HP*	64	0.22	SP*
13	0.27	SP*	39	0.71	MP*	65	4.01	U*
14	0.04	S*	40	1.74	HP*	66	1.49	HP*
15	0.36	SP*	41	0.74	MP*	67	2.15	HP*
16	0.15	S*	42	1.16	HP*	68	2.14	HP*
17	0.34	SP*	43	0.44	SP*	69	0.11	S*
18	0.29	SP*	44	1.13	HP*	70	8.55	U*
19	0.03	S*	45	0.42	SP*	71	2.72	HP*
20	0.36	SP*	46	3.82	U*	72	0.10	S*
21	0.03	S*	47	1.32	HP*	73	0.10	S*
22	0.19	S*	48	0.09	S*	74	1.30	HP*
23	0.19	S*	49	0.08	S*	75	0.15	S*
24	0.17	S*	50	0.41	SP*	76	0.19	S*
25	0.10	S*	51	0.35	SP*	77	0.21	SP*

TABLE 7. Categories of shallow groundwater based on the SPI model results

S*=suitable, SP* =slightly polluted, MP* =moderately polluted, HP* =highly polluted, US* =unsuitable

52

SP*

26

0.20

TABLE 8. Categories of deep groundwater based on the WQI model results

0.15

 S^*

NO.	WQI	Rank	NO.	WQI	Rank	NO.	WQI	Rank
1	28.04	Excellent	20	21.35	Excellent	39	44.71	Excellent
2	30.47	Excellent	21	34.12	Excellent	40	84.60	Good
3	28.77	Excellent	22	67.13	Good	41	92.25	Good
4	61.46	Good	23	20.46	Excellent	42	50.45	Good
5	21.48	Excellent	24	23.96	Excellent	43	51.88	Good

6	60.70	Good	25	20.56	Excellent	44	13.79	Excellent
7	42.46	Excellent	26	333.29	Unsuitable	45	13.49	Excellent
8	45.70	Excellent	27	287.05	Very poor	46	36.43	Excellent
9	35.30	Excellent	28	37.84	Excellent	47	21.85	Excellent
10	49.52	Excellent	29	37.17	Excellent	48	102.99	Poor
11	54.90	Good	30	15.05	Excellent	49	63.51	Good
12	23.08	Excellent	31	48.00	Excellent	50	117.39	Poor
13	19.10	Excellent	32	52.29	Good	51	163.32	Poor
14	19.72	Excellent	33	68.71	Good	52	56.86	Good
15	19.58	Excellent	34	26.14	Excellent	53	36.34	Excellent
16	20.73	Excellent	35	53.63	Good	54	52.44	Good
17	36.08	Excellent	36	23.22	Excellent	55	37.24	Excellent
18	32.06	Excellent	37	67.95	Good	56	36.74	Excellent
19	20.91	Excellent	38	71.86	Good	57	62.98	Good

TABLE 9. Categories of deep groundwater based on the SPI model results

NO.	SPI	Rank	NO.	SPI	Rank	NO.	SPI	Rank
1	0.05	S*	20	0.01		39	0.06	
2	0.01	S*	21	0.01	S*	40	0.13	S*
3	0.06	S*	22	0.15	S*	41	0.11	S*
4	0.06	S*	23	0.01	S*	42	0.08	S*
5	0.01	S*	24	0.02	S*	43	0.07	S*
6	0.13	S*	25	0.02	S*	44	0.01	S*
7	0.03	S*	26	0.35	SP*	45	0.01	S*
8	0.08	S*	27	0.29	SP*	46	0.05	S*
9	0.03	S*	28	0.06	S*	47	0.02	S*
10	0.08	S*	29	0.16	S*	48	0.14	S*
11	0.05	S*	30	0.01	S*	49	0.19	S*
12	0.02	S*	31	0.06	S*	50	0.23	SP*
13	0.01	S*	32	0.07	S*	51	0.30	SP*
14	0.01	S*	33	0.04	S*	52	0.15	S*
15	0.01	S*	34	0.05	S*	53	0.06	S*
16	0.07	S*	35	0.09	S*	54	0.13	S*
17	0.05	S*	36	0.10	S*	55	0.11	S*
18	0.02	S*	37	0.09	S*	56	0.09	S*
19	0.01	S*	38	0.10	S*	57	0.15	S*

 $S^* = suitable, SP^* = slightly \ polluted, MP^* = moderately \ polluted, HP^* = highly \ polluted, US^* = unsuitable$

CONCLUSION

This study explored the factors affecting groundwater chemistry and its quality in detail, and analyzed the hydrogeological processes of shallow groundwater and deep groundwater. In accordance with WHO (2008) guidance, groundwater quality assessments have also been introduced to assess suitability for drinking. The following three conclusions are concluded: First, deep groundwater in aquifers in the study area is weakly alkaline, while that of shallow groundwater is weakly acidic. The abundance for both deep groundwater and shallow groundwater are in the order $HCO_2 > Cl > SO_4^{2-}$ for anions, and $Ca^{2+}>Na^{+}>Mg^{2+}$ for cations, resulting that the water types were dominated by HCO₃-Ca, HCO₃-Ca• Mg, and HCO₂-Ca • Na types. Second, CA and Durov diagram show that rock weathering and dissolution, human activities, and the hydraulic connection between shallow and deep water are the main reasons affecting the chemical composition of water in Helen. At the same time, the high scores of Pb, NO₂⁻, Fe, and Mn must be widely concerned and may become the main environmental geological problems in the area. Third, the analysis of water samples based on the WQI model showed that about 23.37, 23.37, 32.46, 12.98, and 7.79% of the shallow groundwater samples were excellent, good, poor, very poor, and unsuitable for drinking purposes, and that 61.40, 30.90, 5.26, 1.75, and 1.75% of the deep groundwater samples were excellent, good, poor, very poor, and unsuitable for drinking purposes, respectively. The analysis of groundwater samples based on the SPI model showed that 92.98% of the deep groundwater samples were suitable grade, while that 40.25% of the shallow groundwater samples were suitable grade. The spatial distribution maps of the water quality index and the SPI show that most of the deep groundwater resources in the study area are clean and suitable for drinking, despite the risks of the shallow groundwater in the north and southwest of the study area.

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