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RESEARCH ARTICLE

Hydrochemical characterization and quality assessment of groundwater in the hilly area of the Taihang Mountains in Henan Province, China

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Abstract

This study evaluated the quality of groundwater and its suitability for drinking and irrigation in the hilly area of the Taihang Mountains in Henan Province, China. Groundwater samples were collected from 43 unconfined and 20 confined wells and analyzed. The pollution index of groundwater (PIG) was estimated based on the physicochemical parameters, and seven indices, including the sodium adsorption ratio (SAR), sodium percentage (%Na), residual sodium carbonate (RSC), permeability index (PI), magnesium ratio (MR), Kelley's ratio (KR), and corrosivity ratio (CR), were calculated to qualify the groundwater within the research area for irrigation activities. Multivariate statistical techniques were performed to better understand the hydrochemical processes. Chemical analysis showed that the dominant cation and anion were Ca^{2+} and HCO_3^-, respectively, and the principal hydrochemical facies was Ca–Mg–HCO_3. In terms of pH, total dissolved solids, Na^+, Cl^-, F^-, and SO_4^{2-}, most samples were well within the limits prescribed by Chinese standards for drinking water quality, but more than half of the unconfined samples exceeded the specified limits for total hardness and nitrate. The PIG values suggested the pollution level was insignificant for all confined water samples and 72.09% of unconfined water samples, but the PIG distribution map showed that the water in the south central part of the study area had low to moderate pollution. According to the computed values of SAR, %Na, RSC, PI, KR, and MR and the results of a salinity diagram, the results further indicated that most of the studied samples were appropriate for irrigation usage. Only the CR values rendered 41.86% of the unconfined samples and 20% of the confined samples unfit for irrigation. Hence, proper measures are needed to resolve the corrosivity problem. Factor analysis resulted in the extraction of 3 factors that explained 81% of the data variability, and the extracted factors pointed towards geogenic factors governing the groundwater quality.

Keywords Groundwater quality · Hydrochemistry · Risk assessment · Pollution index of groundwater · Factor analysis

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Introduction

In China, the large population, rapidly growing economy, rising water demand, relatively scarce water resources, aging infrastructure, and inadequate governance have together produced water problems that are particularly challenging, and China's per capita availability of renewable water resources is only approximately one-quarter of the global average (Liu and Yang 2012). Understanding the status of water resources in a region is important in water planning and allocation. As an important natural resource, groundwater has several inherent advantages over surface water, such as its wide distribution, negligible evaporation loss, and a lower likelihood of being polluted. Groundwater resources play a critical role in economic development and potable water use in China; groundwater contributes 17.5% of the total water supply (Wang et al.

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2018) and provides drinking water for more than 400 among China's 655 cities (MEP 2011). On the other hand, China has faced groundwater quality problems owing to increasing concentrations of contaminants from either human activities or geological causes (Wang et al. 2018), and it is reported that more than 200 million people in China are still using unsafe water sources (Han et al. 2016). Therefore, keeping drinking water clean is a great public health challenge because of water scarcity and pollution.

Groundwater pollution is one of the most serious problems concerning human survival in the twenty-first century (Li et al. 2014). Groundwater pollution may pose a serious impact on human health, economic development, and social prosperity; hence, it is essential to fully consider the hydrochemical characteristics and groundwater quality for planning and managing groundwater resources reasonably to ensure sustainable safe use. Groundwater quality relies on the nature of the host rock formation, subsurface geochemical processes, topography, soils, atmospheric precipitation, environment, and quality of the recharging water (Balaji et al. 2017). To ensure sustainable groundwater resource development, it is necessary to assess the groundwater quality and determine the origin of hydrochemical variables observed in groundwater. Hydrogeological and geochemical studies are the foundation of groundwater quality evaluation and groundwater resource management, and hydrogeochemical studies are useful in identifying processes that are responsible for groundwater chemistry (Rezaei and Hassani 2018). In the past 10 years, considerable research on drinking or irrigation groundwater quality has been performed in different parts of the world, such as in India (Raju et al. 2011; Thakur et al. 2016; Keesari et al. 2016; Haritash et al. 2017; Kalaivanan et al. 2018; Jain and Vaid 2018; Rezaei and Hassani 2018; Adimalla 2019; Kumar et al. 2020), China (Shi et al. 2013; Li et al. 2014; Ding et al. 2021; Yang et al. 2020), Iran (Jalali 2011; Aghazadeh and Mogaddam 2011; Nematollahi et al. 2018; Mousazadeh et al. 2019), Bangladesh (Islam et al. 2017a, b), the Emirate of Dubai (Ahmed et al. 2019), Ethiopia (Kawo and Karuppannan 2018), Jordan (Abboud 2018), and elsewhere. Among these studies, the sodium adsorption ratio (SAR), sodium percentage (%Na), residual sodium carbonate (RSC), permeability index (PI), Kelley's ratio (KR), magnesium ratio (MR), and corrosivity ratio (CR) are the most commonly used indices to evaluate suitability for irrigation use. The water quality index (WQI) has also been used in judging the water quality in a region (Li et al. 2014; Haritash et al. 2017; Kalaivanan et al. 2018; Kawo and Karuppannan 2018; Adimalla 2019; Mousazadeh et al. 2019).

Although extensive studies have focused on the sustainability of groundwater quality for drinking and irrigation purposes in China, little attention has been paid to groundwater quality in the hilly area of the Taihang Mountains in Henan Province, despite its importance in groundwater recharge and transport in the North China Plain. Only Jiaozuo city, a prefecture-level city rich in mineral resources, has been studied (Huang and Chen 2012; Shi et al. 2013; He et al. 2019). It is therefore highly important to carry out a comprehensive evaluation of groundwater hydrochemistry and its sustainability for domestic and agricultural purposes in the hilly area of the Taihang Mountains in Henan Province. However, earlier studies carried out in this region have not attempted to evaluate and identify the causes of variation in the groundwater quality. We propose an integrated approach involving hydrochemical investigation, pollution index of groundwater (PIG), seven indices, and multivariate statistical analysis to assess the groundwater quality in the hilly area of the Taihang Mountains in Henan Province. In detail, the aims of the present study are to (1) analyze the hydrochemical characteristics of the groundwater and assess the suitability of groundwater quality for drinking purposes using PIG and for agricultural irrigation by employing SAR, %Na, RSC, PI, KR, MR, and CR and to (2) perform cluster analysis (CA) and factor analysis (FA) to identify the main factors affecting the groundwater quality in this area and classify the area into different groundwater quality types. The outcomes of this study will help local residents and decision-makers to take appropriate measures to protect and manage groundwater resources in this area.

Material and method

Study area

The study area is located in the northern part of Henan Province. The hilly and mountainous area in the northern part of Henan Province is part of the eastern foot of the Taihang Mountains, which is located at the junction of the second and third steps of topography in China. Its administrative divisions are related to five prefecture-level cities, including Anyang city, Hebi city, Xinxiang city, Jiaozuo city, and Jiyuan city. The geographical coordinates are 112°02′14″–114°19′47″E and 34°49′22″–36°21′55″N. The Taihang and Zhongtiao Mountains are located in the north and west, loess hills are located in the south and southeast, and an alluvial plain is located in the lower reaches of the Yellow River in the east. There are five types of landforms: mid-elevation mountain, low-elevation mountain, hill, basin, and plain areas.

The study area has a temperate continental monsoon climate. According to the statistical analysis of meteorological data from 22 county (city) meteorological stations in the study area from 1951 to 2013, the annual average temperature is 14.3 °C. The annual average precipitation is 583.8 mm and varies between 148.6 and 1317.4 mm. Precipitation is not evenly distributed in time and space. The precipitation is concentrated mostly in June to September, and this period accounts for more than 70% of the annual precipitation. This kind of precipitation easily causes flood disasters. In contrast, the region is dry in winter and spring, with little rain and snow. The evaporation of the water surface in the study area is 1650–2000 mm. The evaporation in Jiaozuo, Xiuwu, and Qixian in the piedmont region is greater than that in Jiyuan, Wenxian, and Mengzhou along the Yellow River.

Sample collection and analysis

The sampling points were arranged based on the requirements of the standard for investigation and evaluation of groundwater pollution (DD2008-01). The groundwater sampling points included 12 groups in basin and plain areas, two groups in the middle and low mountainous areas, and five groups in the hilly areas arranged every 1000 km^2. Moreover, the number of sampling points was appropriately increased in some areas based on the research requirements. A total of 43 phreatic water (PW) samples and 20 confined water (CW) samples were collected from monitoring wells in the study area from October to November 2014 (Fig. 1). Collected samples were filtered using 0.45-μm membrane filters and stored in polyethylene bottles. The labeled bottles were first washed with concentrated HNO_3, rinsed thoroughly with distilled water, and then rinsed with sample water before sampling. The collection, transport, and testing of samples followed the standard method. Parameters such as air temperature, water temperature, pH, and electrical conductivity (EC) were measured in situ, and other chemical parameters were analyzed in the laboratory.

During analysis, the analytical procedures, quality assurance, and quality control were based on the methods described by the National Standard of the People's Republic of China (GB8538-2008, NHFPC and CFDA 2009). The cations potassium (K^+) and sodium (Na^+) were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) and total hardness (TH), and calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined by the EDTA titrimetric method. Acid titration was used to determine the concentrations of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-). Sulfate (SO_4^{2-}) and chloride (Cl^-) were determined by titrimetric methods. Nitrate (NO_3^-), nitrite (NO_2^-), and fluoride (F^-) were determined by spectrophotometry. Total dissolved solids (TDS) were measured by evaporating prefiltered samples to dryness. Duplicates were conducted for analytical accuracy and quality control, and the accuracy of complete chemical analysis of groundwater samples was measured by assessing the ionic balance error (IBE). The IBE between the total concentrations

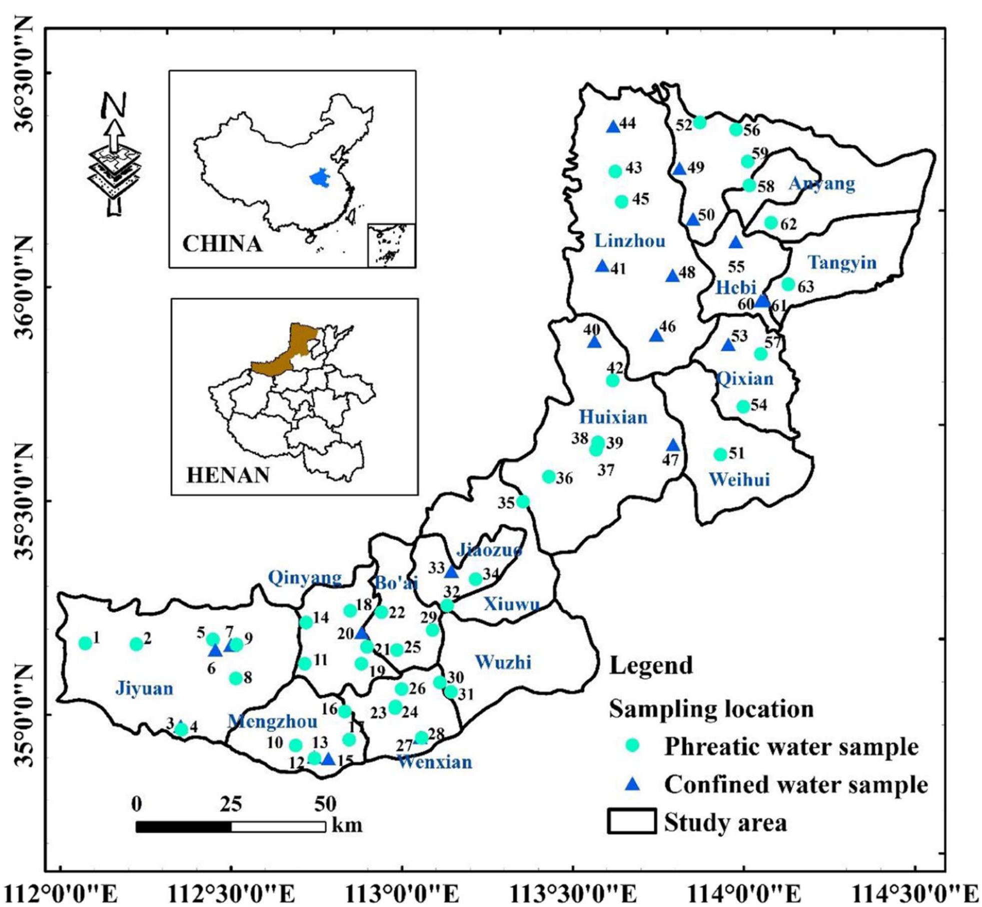


Fig. 1 Location of the study area and the sampling wells

of cations (TCC) and the total concentrations of anions (TCA) expressed in meq/L was calculated for each groundwater sample (IBE = (TCC–TCA)/(TCC + TCA) × 100%, Barzegar et al. 2017). In this study, the IBE values of all samples were less than ±5%, and the correlation coefficient between TCC and TCA was 0.99.

Methods for water quality assessment

Evaluation of groundwater quality for drinking purposes

Based on the values determined during a physicochemical analysis of the collected groundwater samples, the suitability of groundwater as potable water was evaluated by comparing the observed parameter values against the prescribed values of the National Standards for Drinking Water Quality (NSDWQ) (MHPRC and SAPRC 2007) and the WHO (2011) standard. In addition, the PIG was also calculated to represent the quality of drinking water based on the analyzed values of chemical variables.

The PIG is a numerical scale for quantifying the extent of contamination, and it reflects the comprehensive impact of individual water quality measures on the overall water quality of the aquifer (Subba Rao 2012). The PIG is useful for appraising the quality of groundwater for drinking (Subba Rao et al. 2018; Subba Rao and Chaudhary 2019; Marghade et al. 2020). The PIG is calculated by assigning weights to the physicochemical parameters and their influence on the water quality. First, based on the weights assigned by Subba Rao (2012), the relative weights (*Rw*) for all studied parameters are given in Table 1. The *Rw* value for each parameter ranged from 1 to 5 and was assigned per the health influence of the parameter in the study area. The maximum weight of 5 was assigned to TDS, NO_3^-, SO_4^{2-}, and F^-, whereas the minimum weight of 1 was assigned to K^+, as it played a minor role in the evaluation of water quality (Subba Rao 2012). Other parameters, such as TH, Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, and Cl^-, were assigned weights between 1 and 5 depending upon their importance in the water quality evaluation. Second, the weight parameter (*Wp*) of each physicochemical variable was calculated using Eq. (1). Third, each groundwater sample's status of concentration (*Sc*) was estimated according to Eq. (2) by dividing each variable concentration (*C*) by its respective drinking water quality standard (*Ds*), and the values of *Ds* in Table 1 were obtained from the NSDWQ, the standard of the WHO (2011), Subba Rao (2012), and Mousazadeh et al. (2019). Then, the overall water quality (*Ow*) was determined by multiplying *Wp* by the corresponding *Sc*, as shown in Eq. (3). Finally, the PIG value was obtained by summing all *Ow* values of each sample (Eq. (4)); thus, a clear picture of the influence of pollution on aquifer systems is available:

$$Wp_i = Rw_i / \sum_{i=1}^{n} Rw_i \quad (1)$$

$$Sc_i = C_i / Ds \quad (2)$$

$$Ow_i = Wp_i \times Sc_i \quad (3)$$

$$PIG = \sum_{i=1}^{n} Ow_i \quad (4)$$

Subsequently, the computed PIG value of each sample was specified to assess the groundwater quality. A five-grade categorization system was applied to divide the PIG into insignificant, low, moderate, high, and very high pollution for drinking purposes, with the dividing points between classes at 1, 1.5, 2, and 2.5 (Subba Rao 2012).

Table 1 Relative weight (*Rw*) and weight parameter (*Wp*) of each physicochemical parameter, Chinese standard (NSDWQ) and drinking water quality standard (*Ds*)

Parameters	NSDWQ	*Ds*	*Rw*	*Wp*
TDS	1000	1000	5	0.111
TH	450	450	4	0.089
pH	6.5–8.5	7.5	5	0.111
Ca^{2+}		75	2	0.044
Mg^{2+}		50	2	0.044
K^+		12	1	0.022
Na^+	200	200	4	0.089
Cl^-	250	250	4	0.089
SO_4^{2-}	250	250	5	0.111
HCO_3^-		300	3	0.067
NO_3^-		50	5	0.111
F^-	1	1	5	0.111
Total			45	1

Evaluation of groundwater quality for irrigation purposes

Knowledge of irrigation water quality is critical to understand the need for management changes for long-term agricultural productivity (Jalali 2011). With the intention of examining the suitability of groundwater for agricultural irrigation, hydrogeochemical indices, such as SAR, %Na, RSC, PI, KR, MR, and CR, were computed based on measured physicochemical parameters.

Sodium is essential in classifying irrigation water because Na^+ reacts with soil and reduces its permeability (Todd and Mays 2005). SAR and %Na were the most widely used criteria for determining the sodium hazard. The KR is another expression of Na-related hazard that first appeared in Kelley et al. (1940). Further, Eaton (1950) proposed RSC for measuring the hazard related to the use of high-bicarbonate waters, and Doneen (1964) used PI to rate the suitability of groundwater for irrigation purposes. The existence of magnesium is essential to maintaining soil CEC and productivity, but surplus amounts may also be unhealthy (Haritash et al. 2017). Therefore, MR is another investigated index. In addition, CR was employed to determine the extent of the corrosivity of groundwater. All quality indices for irrigation usage are listed in Table 2; note that the ionic concentrations of the used variables are expressed in meq/L.

Results and discussion

Characteristics of groundwater chemistry

The analytical results for all physicochemical parameters of PW and CW groundwater samples in the study area are given in Table 3. The results showed that except for pH, the mean values of all parameters in PW were no less than those in CW samples. Most of the water quality parameters had a high standard deviation (SD), which indicated that groundwater quality might be affected by a variety of hydrochemical processes rather than one process (Islam et al. 2017a). The TH values varied in the range of 254.50–1101.50 mg/L in PW and 100.50–518.50 mg/L in CW samples, with average values of 533.27 and 348.25 mg/L, respectively. The soil texture in the region was predominantly calcareous, which may be the reason for the hardness of the water. The values of TDS in the samples ranged from 322 to 2212 mg/L in PW and 315 to 896 mg/L in CW with average values of 768 and 515 mg/L, respectively. In accordance with the classification of Freeze and Cherry (1979), the TDS values were categorized as freshwater (< 1000 mg/L), brackish water (1000 ~ 10,000 mg/L), saline water (10,000 ~ 100,000 mg/L), and brine water (>100,000 mg/L). The results revealed that all CW samples were within the freshwater category, 76.74% of the PW samples could be considered freshwater type, and the rest of the samples were brackish water. Freshwater may be due to natural soil-rock-water interactions, while brackish water may be an expected result of anthropogenic impact. EC is a good measure of the hazard posed by salinity to crops, as it reflects the TDS in groundwater (Aghazadeh and Mogaddam 2011). Wide variation in EC was observed, from 10.35 to 2707 μS/cm with an average value of 1025 μS/cm in PW and from 507 to 1173 μS/cm with an average value of 757 μS/cm in CW. The large differences in EC values reflect large differences in geochemical approaches predominant in the study area (Abboud 2018). In the PW and CW samples, the pH ranges were 7.20–7.95 and 7.30–8.10, with average values of 7.65 and 7.68, respectively. These results suggest that the groundwater was generally neutral to alkaline. This variation may be due to the influence of chemical fertilizer from farmlands and the leaching of dissolved constituents into the groundwater (Islam et al. 2017a).

The order of abundance of the major cations and anions is depicted in violin plots (Fig. 2). Clearly, in both PW and CW samples, the abundance of cations varied in the order $Ca^{2+} > Mg^{2+} > Na^+ > K^+$, while the abundance of anions varied in the order $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > F^-$. Mao et al. (2021) reported that the most dominant cation and anion in the groundwater of the east foothills of the Taihang Mountains, Hebei Province, were Ca^{2+} and HCO_3^- ions, respectively, with the same abundance order of the major ions. Huang and Chen (2012) and Jiang et al. (2016) also reported that the dominant cation and anion in the groundwater of Jiaozuo city and Linzhou city were Ca^{2+} and HCO_3^-, respectively. In PW samples, Ca^{2+}, Mg^{2+}, HCO_3^-, and SO_4^{2-} showed the largest variability, while K^+, F^-, NO_3^-, and Cl^- showed the smallest variability; in CW samples, Na^+ and Ca^{2+} showed the largest variability, and K^+, F^-, NO_3^-, and Cl^-showed the smallest variability. The variation in the parameters of PW was larger than that of CW, indicating that the hydrochemical properties of PW were highly variable in space and were

Table 2 Hydrogeochemical indices employed in assessing groundwater used for irrigation

Index	Equation	References
Sodium adsorption ratio	$SAR = Na^+/\sqrt{(Ca^{2+}+Mg^{2+})/2}$	Richards (1954)
Sodium percentage	$\%Na = 100 \times \frac{Na^+}{Na^++K^++Ca^{2+}+Mg^{2+}}$	Wilcox (1948)
Residual sodium carbonate	$RSC = (CO_3^{2-}+HCO_3^-) - (Ca^{2+}+Mg^{2+})$	Eaton (1950)
Permeability index	$PI(\%) = 100 \times \frac{Na^++\sqrt{HCO_3^-}}{Na^++Ca^{2+}+Mg^{2+}}$	Doneen (1964)
Kelley's ratio	$KR=Na^+/(Ca^{2+}+Mg^{2+})$	Kelley et al. (1940)
Magnesium ratio	$MR=100\times Mg^{2+}/(Ca^{2+}+Mg^{2+})$	Raghunath (1987)
Corrosivity ratio	$CR = \frac{Cl^-/35.5+2\times(SO_4^{2-}/96)}{2\times(HCO_3^-+CO_3^{2-})}/100$	Tripathi et al. (2012)

Note: all ionic concentrations are in meq/L

Table 3 Statistics of chemical parameters in groundwater for phreatic water (PW) and confined water (CW) samples

	PW			CW		
	Mean	Range	SD	Mean	Range	SD
TH	533.27	254.50–1101.50	209.92	348.25	100.50–518.50	90.40
TDS	768	322–2212	420	515	315–896	127
EC	1025	10.35–2707	584	757	507–1173	166
pH	7.65	7.20–7.95	0.21	7.68	7.30–8.10	0.23
Ca^{2+}	132.65	47.49–251.30	46.87	93.59	26.05–154.71	30.20
Mg^{2+}	50.76	15.80–204.36	42.08	27.01	8.63–54.19	11.00
K^{+}	1.62	0.23–16.19	2.53	1.62	0.46–4.45	1.06
Na^{+}	58.77	4.41–349.60	76.05	43.19	2.55–160.80	48.35
Cl^{-}	76.72	12.05–260.56	64.23	37.20	10.28–67.71	18.94
SO_4^{2-}	181.02	23.05–1082.60	199.09	108.21	40.35–335.73	67.66
HCO_3^{-}	370.43	212.96–749.33	111.74	306.17	216.62–421.65	55.01
NO_3^{-}	64.92	0.26–186.30	54.72	28.93	0.03–61.94	20.32
F–	0.36	0.05–1.72	0.36	0.35	0.05–2.48	0.56

Note: all values are in mg/L except for pH, which is dimensionless, and EC in μS/cm

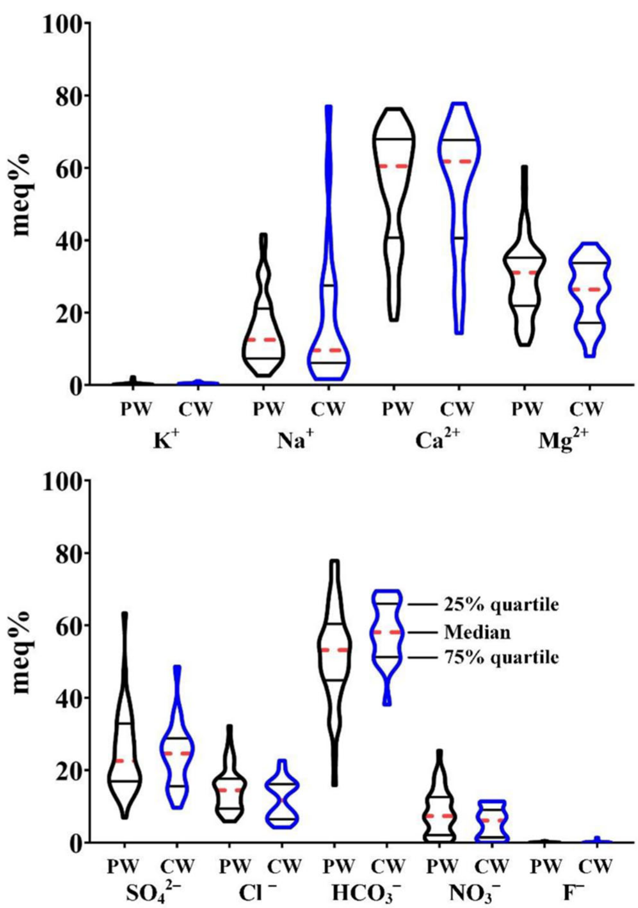


Fig. 2 Violin plots of major cation and anion proportions in PW and CW samples, respectively

greatly influenced by aquifer media, topography, hydrometeorological conditions, and human activities, while CW was less disturbed by external factors.

Calcium is an abundant cation in natural water and mainly originates from carbonate minerals (calcite and dolomite) and plagioclase feldspar (Keesari et al. 2016). The dominant cation Ca^{2+} concentrations ranged from 47.49 to 251.30 and 26.05 to 154.71 mg/L in PW and CW with average values of 132.65 and 93.59 mg/L, respectively (Table 3). Mg^{2+}, Na^{+}, and K^{+} are also common cations in natural waters. The concentrations of K^{+}, Na^{+}, and Mg^{2+} in PW varied from 0.23 to 16.19, 4.41 to 349.60, and 15.80 to 204.36 mg/L with mean values of 1.62, 58.77, and 50.76 mg/L, respectively. In CW, the ranges of the three ions were smaller than those in PW, with lower mean concentrations of 1.62, 43.19, and 27.01 mg/L for K^{+}, Na^{+}, and Mg^{2+}, respectively. Total alkalinity in water is mainly caused by OH^{-}, CO_3^{2-}, and HCO_3^{-} ions. The mean concentrations of HCO_3^{-} were 370.43 mg/L in PW and 306.17 mg/L in CW in the study region (Table 3). Singh and Tripathi (2016) pointed out that if the concentration of $HCO_3^{-} > 300$ mg/L, HCO_3^{-} may be contributed by carbonate dissolution because carbonic acid can form as a result of infiltrating carbon dioxide. The SO_4^{2-} concentrations in the groundwater varied from 23.05 to 1082.60 mg/L, with a mean of 181.02 mg/L, and from 40.35 to 335.73 mg/L, with a mean of 108.21 mg/L, in PW and CW, respectively. High contents of SO_4^{2-} in PW may be derived from the dissolution of gypsum or the oxidation of sulfide minerals, wastes resulting from domestic activities, and agricultural runoff (fertilizers). Cl^{-} and F^{-} are common anions in groundwater. The concentrations of Cl^- and F^- varied from 12.05 to 206.56 mg/L and 0.05 to 1.72 mg/L in PW and from 10.28 to 67.71 mg/L and 0.05 to 2.48 mg/L in CW, respectively (Table 3). The natural source for Cl^- may be the dissolution of rock salt or other chlorides, and the higher concentration of Cl^- in PW than CW may be caused by the process of removal of other ions from the system by adsorption or result from pollution by domestic sewage wastes. Nitrate is considered to be the most widespread contaminant in groundwater in Henan Province (Zhang et al. 2014; Jiang et al. 2016; Wang et al. 2017). The NO_3^- concentration in groundwater in the study region ranged from 0.26 to 186.3 mg/L and 0.03 to 61.94 mg/L, with means of 64.92 mg/L and 28.93 mg/L in PW and CW, respectively (Table 3).

Hydrochemical evaluation

To understand the hydrochemistry of groundwater, GW_Chart Software (USGS) was used to generate a Piper diagram. Piper ternary diagrams (Piper 1944) are extensively used to interpret hydrochemical facies and can be used to evaluate the chemical processes and evolution of groundwater in aquifers (Thakur et al. 2016; Barzegar et al. 2017; Adimalla 2019; Yang et al. 2020). Obviously, most samples fall into subfields I and II, which are characterized by Ca–Mg–HCO_3 and Ca–Mg–Cl–SO_4 types of facies, while the Na–K–Cl–SO_4 type is absent (Fig. 3). Most of the samples fall within zone 1 and zone 3, illustrating that alkaline earth ions (Ca^{2+} and Mg^{2+}) exceed alkaline ions (Na^+ and K^+) and that weak acids (HCO_3^- and CO_3^{2-}) exceed strong acids (Cl^- and SO_4^{2-}), suggesting that Ca^{2+} and HCO_3^- contribute greatly to the hydrochemical compositions (Fig. 3 and Table 4). Figure 3 also demonstrates that most of the samples are distributed through zone 5 and zone 9, which represent the presence of temporary hard water and permanent hard water in the study area, of which Ca–Mg–HCO_3 was the predominant facies type. Ca–Mg–HCO_3 may be mainly ascribed to the dissolution of carbonate minerals, which are very common in the study area. Negligible examples of the Ca–Mg–SO_4 type (1 PW sample) and Na–HCO_3 type (2 CW samples) were also observed. In the lowerleft cation triangle, the Ca type and nondominant type of groundwater dominated in the study area. In the lower right anion triangle, the HCO_3 type was prominent (Table 4).

The Langelier-Ludwig (1942) diagram is also implemented to assess the groundwater quality and determine the controlling mechanism of groundwater hydrochemistry. The diagram represents four parts, and each part is separated by 50% of the

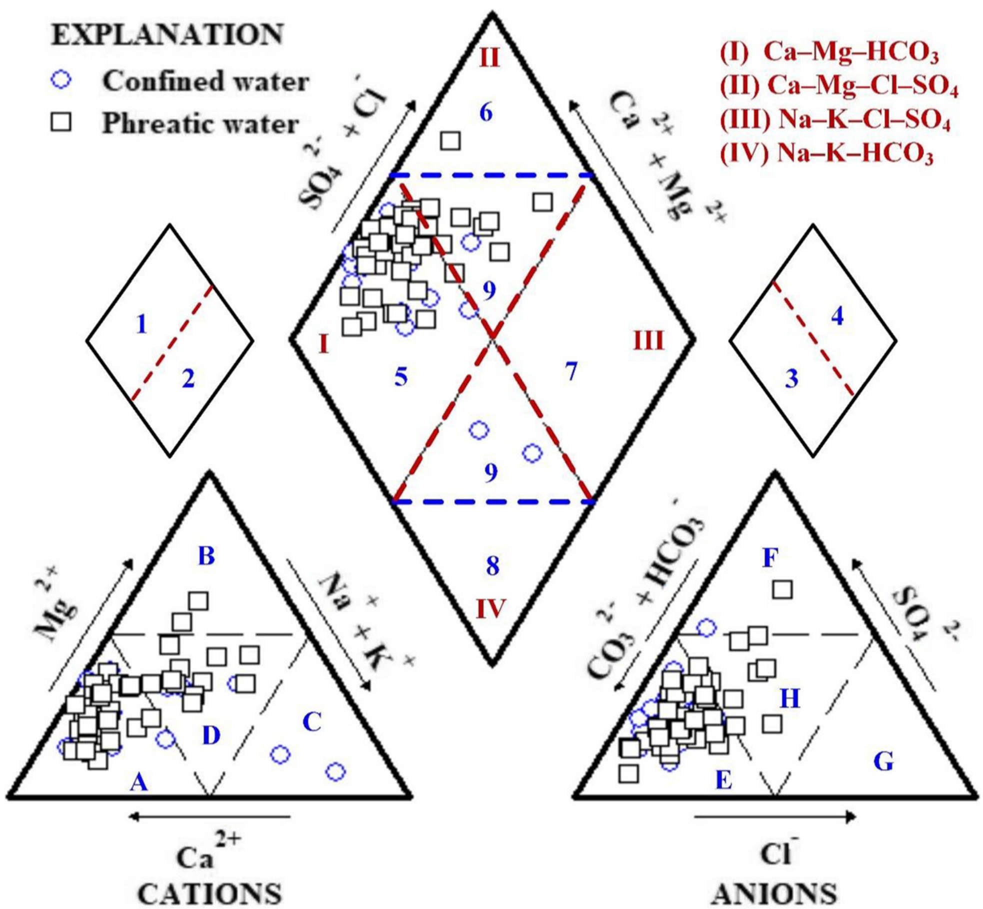


Fig. 3 Classification of hydrochemical facies on Piper plot

Table 4 Geochemical characteristics and groundwater types in Piper's diagram

Zone	Sample in the zone (%)	
	PW	CW
(1) Alkaline earths exceed alkalis	100	90
(2) Alkalis exceed alkaline earths	0	10
(3) Weak acids exceed strong acids	74.42	95
(4) Strong acids exceed weak acids	25.58	5
(5) Ca–Mg–HCO_3	74.42	85
(6) Ca–Mg–SO_4	2.33	0
(9) Mixed type	23.25	15
(A) Ca type	69.77	70
(B) Mg type	4.65	0
(C) Na+K type	0	10
(D) Nondominant type	25.58	20
(E) HCO_3 type	74.42	95
(F) SO_4 type	2.33	5
(G) Cl type	0	0
(H) Nondominant type	23.26	0

total ions (Fig. 4). The counted percentages of K^++Na^+, Ca^{2+}+ Mg^{2+}, HCO_3^- + CO_3^{2-}, and Cl^- + SO_4^{2-} varied from 1.81 to 77.71, 22.29 to 98.19, 40.64 to 76.13, and 23.87 to 59.36 for CW and from 2.70 to 41.83, 58.17 to 97.30, 15.85 to 82.94, and 17.06 to 84.15 for PW, respectively. In total, 85% of CW samples and 74.42% of PW samples plot in the meteoric water zone with a Ca–Mg–HCO_3 composition (Fig. 4). Only one CW sample and the remaining 25.58% of PW samples plot in the area of Ca–Mg–Cl–SO_4 composition. Two CW samples fall in the area of the Na–K–HCO_3 type, and these relatively high concentrations of Na^++K^+ and HCO_3^- may have resulted from mineral dissolution and the absorption of large amounts of CO_2 during infiltration of recharge water (Abboud 2018).

Evaluation of groundwater quality

Appraisal of PIG

PIG reflects various composite influences of individual water quality parameters on the overall quality of water for drinking purposes. The computed PIG values varied from 0.43 to 0.86 and 0.39 to 1.88 for the CW and PW samples, respectively. The calculated PIG for individual samples is represented in Fig. 5. It was evident that all CW samples represented insignificant pollution (PIG<1.0), and with regard to the PW samples, 72.09% of samples were categorized as insignificant

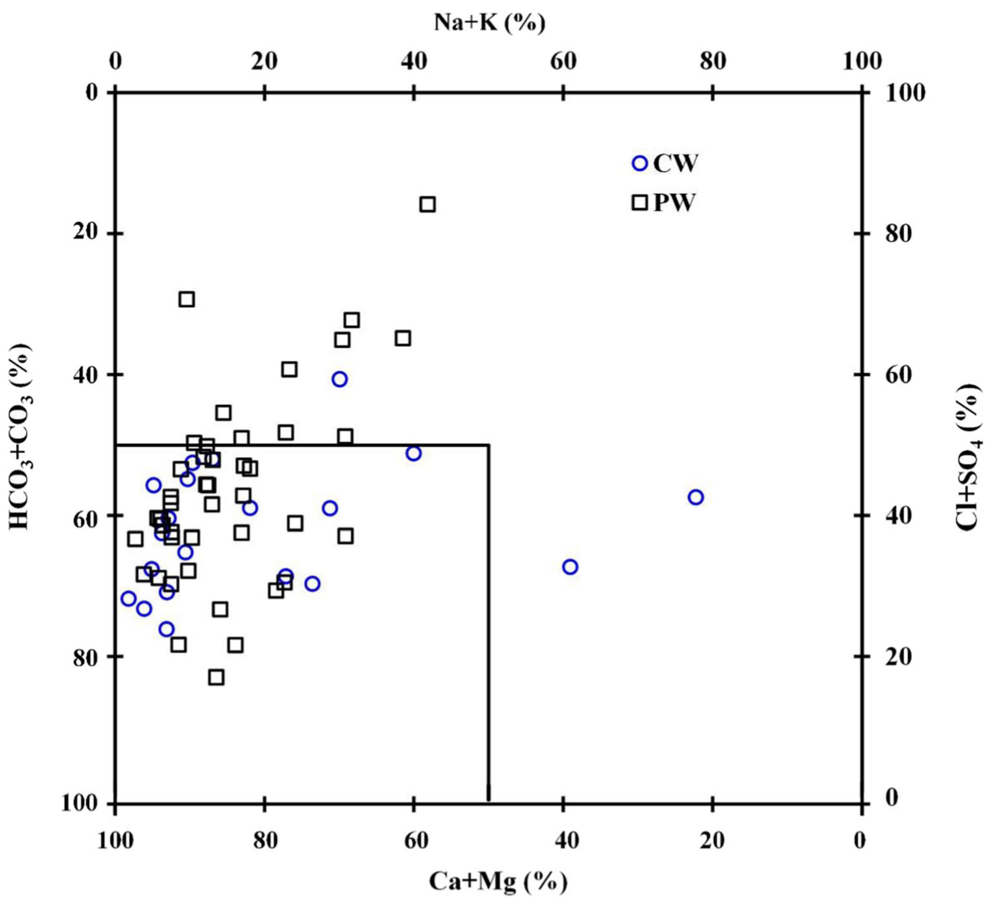


Fig. 4 Langelier-Ludwig diagram for groundwater samples in the study area

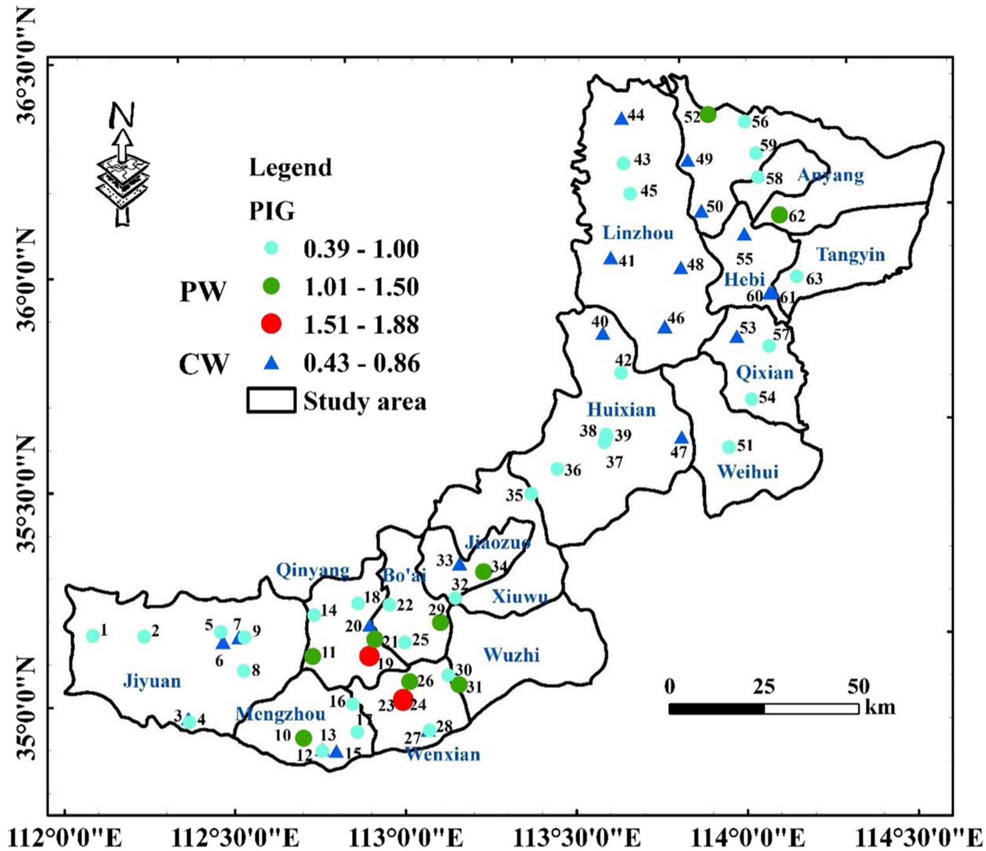


Fig. 5 Spatial distribution maps for pollution index of groundwater in both confined and unconfined aquifers

pollution, and 20.93% of samples were categorized as low pollution (1.0 < PIG <1.5); only 6.98% of samples were categorized as moderate pollution (1.5 < PIG < 2.0), and no samples were categorized as high pollution (2.0 < PIG <2.5) or very high pollution (PIG >2.5). Obviously, the CW samples exhibited better quality than the PW samples. Among all samples, the water quality of samples 10, 11, 21, 26, 29, 31, 34, 52, and 62 was categorized as low pollution; these samples were concentrated in the south and central part and in Anyang county, and these sample locations were surrounded by a landfill, mineral waste residue, septic tanks, and livestock farms. Moderate pollution was found in locations 19, 23, and 24 in Qinyang and Wenxian counties, which may be the influence of septic tanks and domestic activities. It should be noted that water treatment is needed when drinking water is collected from these three moderate pollution wells; otherwise, the public will suffer from water-borne diseases.

As shown in Table 5, there was little difference in *Ow* values with respect to pH and K^+ among all pollution zones, which meant these two parameters were not the key factors in identifying the pollution zones. In the insignificant pollution zone, the CW samples' pH and PW samples' pH and NO_3^- possessed average values of *Ow* greater than 0.1. While the other parameters were characterized by *Ow* values less than 0.1, these parameters were regarded as nominal contributors to natural groundwater quality (Subba Rao 2012). For the PW

Table 5 Identification of samples into classified pollution zones based on the pollution index of groundwater

	Confined water				Unconfined water			
	IP		IP		LP		MP	
	Ow	*C*	*Ow*	*C*	*Ow*	*C*	*Ow*	*C*
PIG	0.57		0.66		1.15		1.70	
TDS	0.06	515.37	0.06	566.91	0.12	1054.69	0.22	1989.54
TH	0.07	348.25	0.08	424.81	0.14	733.33	0.21	1053.83
pH	0.11	7.68	0.11	7.64	0.11	7.66	0.12	7.78
Ca^{2+}	0.06	93.59	0.07	117.43	0.11	177.67	0.09	154.88
Mg^{2+}	0.02	27.01	0.03	33.55	0.06	70.49	0.15	169.45
Na^+	0.02	43.19	0.01	30.20	0.03	76.93	0.13	299.47
K^+	0.00	1.62	0.00	1.20	0.01	2.87	0.00	2.12
HCO_3^-	0.07	306.17	0.07	329.71	0.10	449.85	0.12	553.05
Cl^-	0.01	37.20	0.02	46.45	0.04	125.57	0.09	242.95
SO_4^{2-}	0.05	108.21	0.05	106.05	0.10	235.56	0.35	792.01
NO_3^-	0.06	28.93	0.11	50.49	0.27	120.28	0.11	47.95
F^-	0.04	0.35	0.03	0.29	0.05	0.44	0.10	0.94

IP, LP, and MP mean insignificant pollution, low pollution, and moderate pollution, respectively. Concentrations in mg/L except for pH dimensionless samples, the TDS, TH, pH, Ca^{2+}, SO_4^{2-}, and NO_3^- yielded *Ow* values higher than 0.1 in the low-pollution zone. The *Ow* values of these six parameters were not lower than the corresponding values in the insignificant pollution zone. The groundwater quality occurring in the moderate pollution zone corresponded to *Ow* values of TDS, TH, pH, Mg^{2+}, Na^+, HCO_3^-, SO_4^{2-}, NO_3^-, and F^- greater than 0.1. In the unconfined aquifer, there was a gradual increase in the *Ow* values of TDS along with those of TH, Mg^{2+}, Na^+, HCO_3^-, Cl^-, SO_4^{2-}, and F^- from the insignificant to moderate pollution zones, leading to an increase in the ionic strength. The low- and moderate-pollution zones identified by PIG exhibited NO_3^- (0.27) and SO_4^{2-} (0.35) enrichment in the groundwater (Table 5). Furthermore, it can also be observed from Table 5 that the moderate pollution groundwater quality column is associated with higher average values of TDS, TH, pH, Mg^{2+}, Na^+, HCO_3^-, Cl^-, SO_4^{2-}, and F^-, than the low-pollution groundwater quality column. It is remarkable that the average Ca^{2+} (154.88 mg/L) and NO_3^- (47.95 mg/L) contents in the moderate pollution groundwater quality column were less than those (Ca^{2+} and NO_3^- concentrations of 177.67 and 120.28 mg/L, respectively) in the low-pollution groundwater quality column. This difference could be attributed to variation in the source of pollution in the groundwater system.

Suitability for drinking purposes

To assess the suitability of groundwater for drinking purposes, the results of the parameters of groundwater samples were compared with the NSDWQ (MHPRC and SAPRC 2007) for drinking water (Table 1). The pH values of all samples were within the permissible limits of the NSDWQ. Hard water was generally unsuitable for domestic use, as per the NSDWQ, in approximately 46.51% of PW samples and 95.00% of CW samples, and TH fell within the acceptable limit of 450 mg/L. Most of the samples (76.74% in PW and 100% in CW) were found to be within the acceptable limit of 1000 mg/L of TDS, but Indian standard specifications for drinking water reported that water with TDS > 500 mg/L may cause gastrointestinal irritation and is not suitable for drinking water supplies (Jain and Vaid 2018). The cations K^+, Na^+, Ca^{2+}, and Mg^{2+} did not have any prescribed limits for drinking water, but high levels of sodium in drinking water make it salty in nature. High Na^+ concentrations in drinking water may pose a risk to persons suffering from cardiac, renal, and circulatory diseases (WHO 2011). The prescribed limit of Na^+ in the NSDWQ is 200 mg/L, and only approximately 6.98% of PW samples had Na^+ concentrations above the acceptable limits, while the remaining samples were within the prescribed limits. No health-based guideline value has been established for HCO_3^-. The maximum allowable limit for Cl^- and SO_4^{2-} concentrations in drinking water is 250 mg/L in the NSDWQ. The concentrations of Cl^- in all CW samples were within the permissible limits, and only two PW samples exceeded the standard. For SO_4^{2-}, approximately 95.00% of CW samples and 81.40% of PW samples showed values lower than the prescribed standard. Due to its solubility and mobility, NO_3^- is prone to leaching through soils with infiltrating water, i.e., NO_3^- is leached by rainfall or irrigation water (Jalali 2011). The presence of high nitrate concentrations in drinking water may result in methemoglobinemia in infants. Nitrate is often regarded as a good indicator of anthropogenic influence on the groundwater environment (Ahmed et al. 2019). In terms of NO_3^- contamination, 20% of CW samples and 55.81% of PW samples exhibited values above the WHO maximum recommended limit, i.e., 50 mg/L (WHO 2011) making them unsafe for drinking purposes. F^- is attracted by Ca^{2+} in teeth and bones because of its strong electronegativity, so excessive intake can lead to pathological changes in teeth and bones, such as mottling of teeth or dental fluorosis followed by skeletal fluorosis (Keesari et al. 2016). In the study area, only 10% of CW samples and 6.98% of PW samples exceeded the NSDWQ and hence were not suitable for drinking. When $F^- < 0.2$ mg/L, water should be pretreated, and fluoride is usually added to drinking water to help prevent tooth decay in children (Abboud 2018). The F^- concentrations of 50% of CW samples and 34.88% of PW samples were less than 0.2 mg/L, and these water sources should be treated when used for potable use.

In summary, most of the groundwater quality of the study area is suitable for drinking, but when the groundwater is used for drinking, the TH and nitrate contamination should be noted.

Suitability for irrigation purposes

SAR is a measure of the sodium/alkali hazard to crops and reflects the extent of adsorption of sodium by soils; hence, it is a crucial index for evaluating the suitability of groundwater for irrigation (Rezaei and Hassani 2018). The higher the SAR, the greater the risk of sodium damage to plant growth. The values of SAR in the groundwater of the study area varied from 0.11 to 4.66 in PW samples and 0.06 to 6.95 in CW samples. The SAR value of all groundwater samples was < 10, indicating the excellent groundwater quality for agricultural purposes, as classified by Richards (1954) (Table 6). In the US Salinity Laboratory (USSL) diagram (Fig. 6), the salinity hazard was divided into C1, C2, C3, and C4 classes, the sodium hazard was classified into the classes S1, S2, S3, and S4, and the dividing points between classes are depicted in Table 6. Clearly, three PW samples belong to the C4 class (EC >2250 μS/cm), indicating very high salinity with low to medium sodium, making them unfit for irrigation under ordinary conditions but possibly useful under some special conditions (Richards 1954). One CW sample plots in the C3S2 class, indicating a high salinity and

Table 6 Criteria for classification of groundwater quality for irrigation usage

Quality	SAR	EC	%Na	RSC	PI%	KR	MR	CR
Excellent	0–10	<250	<20					
Good	10–18	250–750	20–40	<1.25	75–100	<1	<50%	<1
Permissible	18–26	750–2000	40–60					
Doubtful		2000–3000	60–80	1.25–2.5	25–75			
Unsuitable	>26	>3000	>80	>2.5	<25	>1	>50%	>1

medium sodium hazard, and this type of water cannot be used on soils with restricted drainage but may be used on coarse-textured or organic soils with good permeability (Raju et al. 2011). Most groundwater samples plot in the categories of C2S1 (50% of CW samples and 25.58% of PW samples) and C3S1 (45% of CW samples and 62.79% of PW samples), signifying medium to high salinity with low sodium concentrations, and these types have been deemed suitable for irrigation on almost all types of soil with little danger of exchangeable sodium (Dar et al. 2011). In addition, two PW samples are located in the C1S1 (low salinity and low sodium) water type and can be used for irrigation of most crops on most soils.

The calculated %Na for groundwater in the study area was plotted against EC, as shown in Fig. 7. The categorizations of groundwater on the basis of %Na and EC are listed in Table 6. Wilcox's diagram (1948) was applied to assess groundwater quality for irrigation, and the diagram provided the apparent

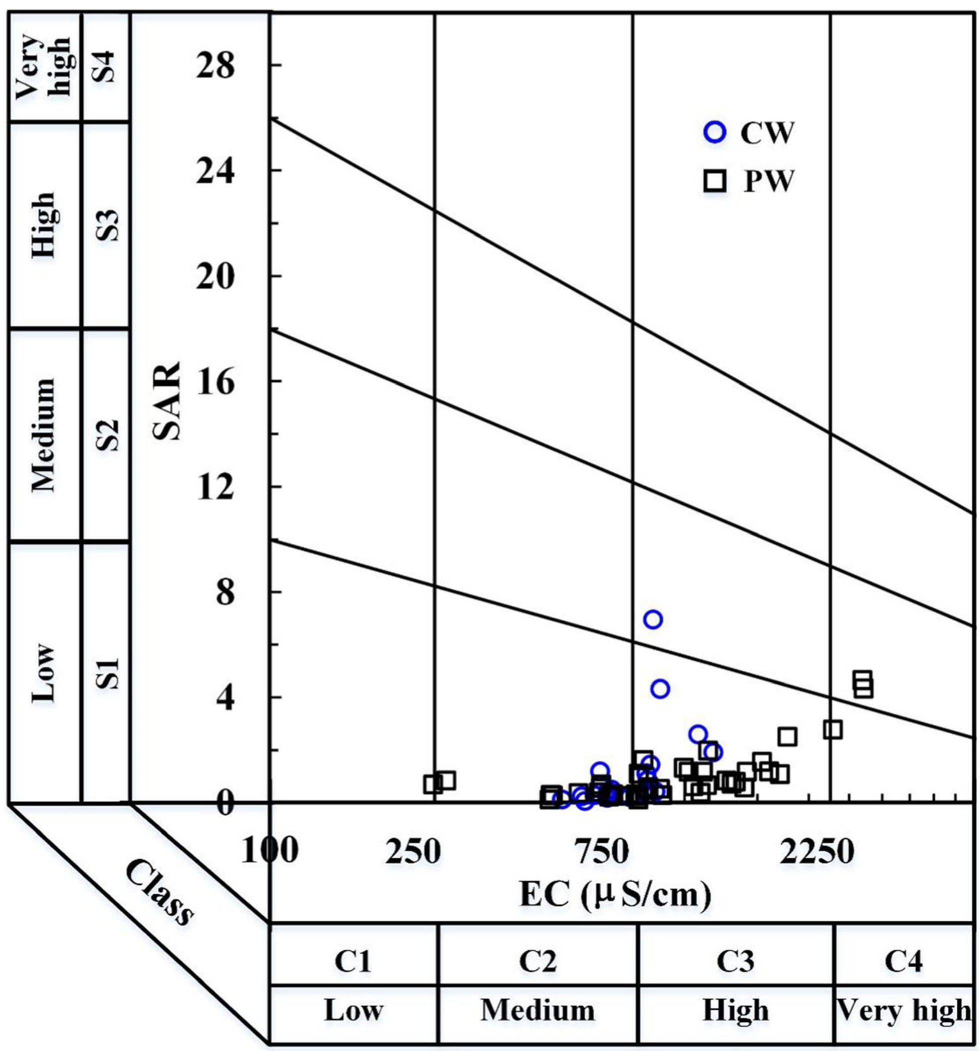


Fig. 6 Classification of irrigation water quality, with respect to salinity hazard and sodium hazard

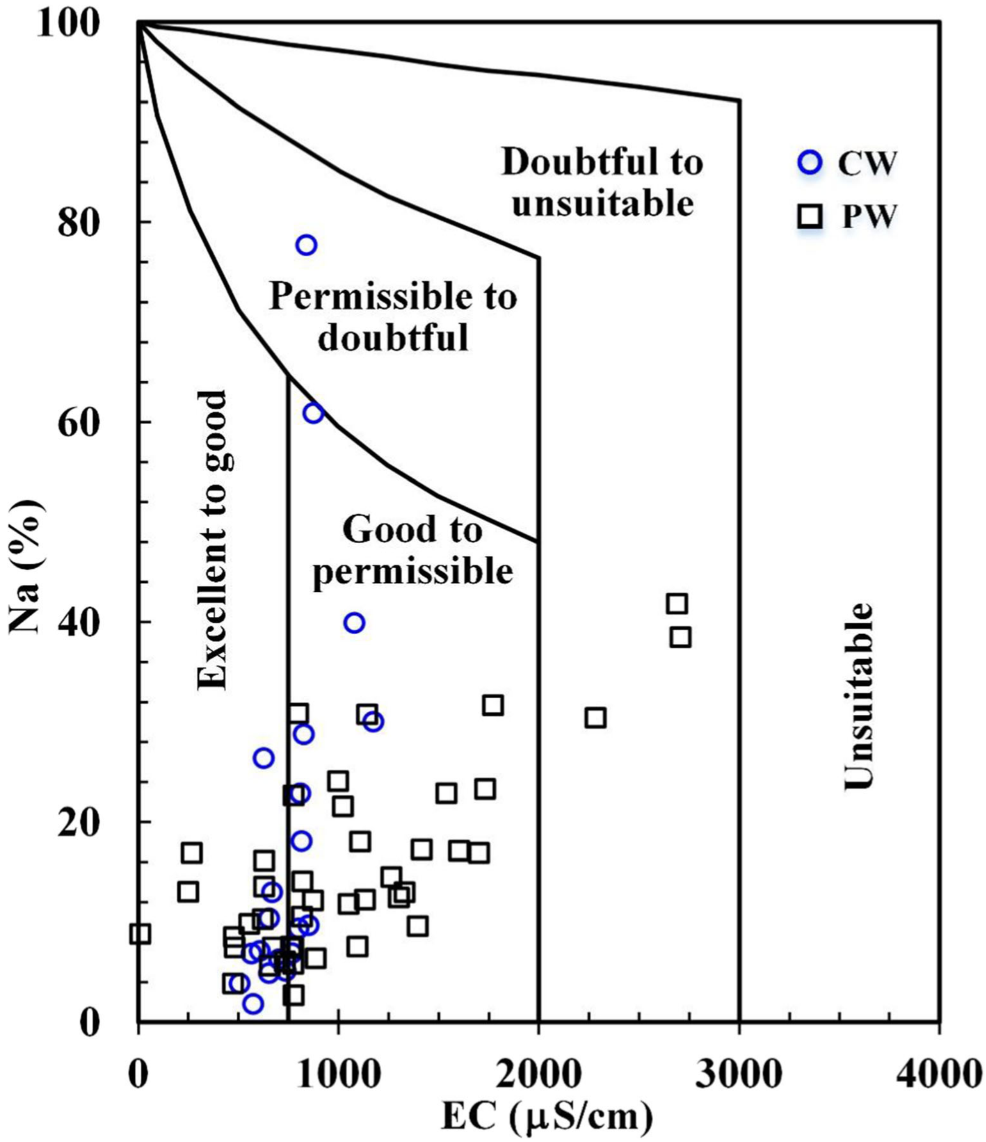


Fig. 7 Classification of irrigation waters (after Wilcox 1948)

situation for understanding the suitability of water for irrigation (Balaji et al. 2017). The %Na varied in the range of 2.70–41.83% in PW samples and 1.81–77.71% in CW samples. Most of the samples corresponded to the categories of excellent to good and good to permissible and can be used for irrigation. Only one CW samples fell in the permissible to doubtful category, three PW samples fell in the doubtful to unsuitable category, and no samples were considered unsuitable for irrigation. Hence, based on Wilcox's diagram, most groundwater samples were fit for irrigation.

The classification of irrigation water based on RSC values is also presented in Table 6. The RSC computed for the study area ranged from −15.64 to 3.38 (mean = −3.38) meq/L. According to the categorization, all PW samples and 90% of the CW samples were less than 1.25 meq/L, suggesting that the groundwater of the study area was good for irrigation. Only 10% of the CW samples had high RSC values (> 2.5 meq/L) indicating the increase of the adsorption of Na^+ in soil and the decrease of the permeability of the soil and unsuitable for plant growth (Yang et al. 2020). The results imply that the groundwater in the study area is of good quality for irrigation uses.

Based on PI, the quality of water can be categorized into three classes (Table 6): greater than 75%, between 25% and 75%, and less than 25% for classes I, II, and III, meaning suitable, marginally suitable, and unsuitable for irrigation, respectively. The PI varied from 21.49% to 55.13% for PW samples and 28.47% to 103.36% for CW samples. The results showed that two CW samples were assigned to class I, one PW sample was assigned to class III, and the remaining samples were considered marginally suitable for irrigation. This indicated that except for one PW well, all water is suitable for irrigation uses in the study area.

Similarly, the KR has been calculated from the groundwater samples, and it ranged from 0.017 to 3.46 and from 0.026 to 0.714 for CW and PW samples, respectively. In view of the criteria in Table 6, the KR values of all PW samples and 90% of the CW samples were < 1, which suggested that these samples were good for irrigation, and only the remaining 10% of the CW samples were regarded as unsuitable for irrigation.

Jalali (2011) reported that a given SAR value will show slightly more damage if the $Ca^{2+}/Mg^{2+} < 1$. MR and this ratio are mathematically equivalent. The MR ranges of PW and CW samples in the study area were 16.41–58.10% and 13.37–72.93%, respectively. According to the MR classification (Table 6), approximately 5% of CW samples and 18.60% of PW samples were unsuitable for irrigation.

If the groundwater samples have a CR value of less than 1, the groundwater is deemed safe for transport by pipes, whereas if the groundwater samples have a CR value >1, the water is considered corrosive and cannot be transported through metal pipes (Tripathi et al. 2012). The calculated CR values varied between 0.26 and 6.01 for PW samples and 0.37 and 1.59 for CW samples. The results indicate that 20% of the CW samples and 41.86% of the PW samples were corrosive and needed noncorrodible pipes to transport and extract the groundwater.

In summary, most groundwater in the study area is suitable for irrigation usage, but noncorrodible (such as polyvinyl chloride) transportation pipes should be selected.

Statistical analysis and source analysis

Correlation analysis

The degree of a linear relationship between two variables was evaluated using Pearson correlation analysis, which is a widely used statistical measure. To identify the relationship between different variables and the sources of dissolved salts in the groundwater, the correlation matrices for 13 variables were prepared for both CW and PW samples (Table 7) by SPSS 23 to compute the Pearson correlation coefficient (r). For PW samples, strong correlations were observed for TH–TDS, TH–EC, TH–Mg^{2+}, TH–Na^+, TH–Cl^-, TH–SO_4^{2-}, TDS–EC, TDS–Mg^{2+}, TDS–Na^+, TDS–Cl^-, TDS–SO_4^{2-}, EC–Mg^{2+}, EC–Na^+, EC–Cl^-, and EC–SO_4^{2-}, which revealed that the presence of TH, Na^+, Mg^{2+}, Cl^-, and SO_4^{2-} greatly influenced the EC and TDS and that the hardness strongly depended on Mg^{2+}, Na^+, Cl^-, and SO_4^{2-}. In addition, highly significant positive correlations between different ions, such as Mg^{2+}–Na^+, Mg^{2+}–SO_4^{2-}, Na^+–Cl^-, and Na^+–SO_4^{2-}, are also shown in Table 7, indicating that these four ions might have the same source. Additionally, TH–Ca^{2+}, TH–HCO_3^-, TH–F^-, TDS–Ca^{2+}, TDS–HCO_3^-, TDS–F^-, EC–Ca^{2+}, EC–HCO_3^-, EC–F^-, Ca^{2+}–Cl^-, Ca^{2+}–NO_3^-, Mg^{2+}–Cl^-, Mg^{2+}–HCO_3^-, Mg^{2+}–F^-, Na^+–HCO_3^-, Na^+–F^-, Cl^-–SO_4^{2-}, Cl^-–HCO_3^-, SO_4^{2-}–HCO_3^-, SO_4^{2-}–F^-, and HCO_3^-–F^- exhibited significant positive correlations ranging between 0.4 and 0.8. The strong correlations of Na^+ with Cl^- and SO_4^{2-} and the significant positive correlation between Cl^- and SO_4^{2-} indicate the influences of evaporation, agricultural activities, and poor drainage conditions on the groundwater system. Except for F^-, no significant correlation with pH was observed for any of the studied variables.

The results of the correlation matrix in CW samples were different from those in PW samples. In CW samples, only TH–Ca^{2+}, TDS–EC, TDS–SO_4^{2-}, Ca^{2+}–NO_3^-, and Na^+–F^- were strongly correlated. Significant positive correlations for TDS–K^+, TDS–Na^+, TDS–HCO_3^-, EC–K^+, EC–Na^+, EC–SO_4^{2-}, EC–HCO_3^-, K^+–Na^+, K^+–SO_4^{2-}, K^+–HCO_3^-, and Na^+–HCO_3^- at the 0.01 level and TH–Mg^{2+}, TH–NO_3^-, EC–Cl^-, and Na^+–SO_4^{2-} at the 0.05 level were also observed. Notably, significant negative correlations were found for TH–pH ($r = -0.569$), TH–F^- ($r = -0.731$), pH–Ca^{2+} ($r = -0.693$), and Ca^{2+}–F^- ($r = -0.675$) at the 0.01 level and TH–Na^+ ($r = -0.452$), Na^+–Ca^{2+} ($r = -0.502$), Na^+–NO_3^- ($r = -0.497$), pH–NO_3^- ($r = -0.494$), and F^-–NO_3^- ($r = -0.465$) at the 0.05 level. The poor correlation between Mg^{2+} and Na^+ and the negative correlation between Na^+ and Ca^{2+} may be caused by the replacement of Ca^{2+} or Mg^{2+} in groundwater with Na^+ in aquifer materials. The poor correlation between NO_3^- and Mg^{2+} and the negative correlation between NO_3^- and Na^+ indicate that NO_3^- could be derived from agricultural activities (Kawo and Karuppannan 2018).

Cluster analysis

Hierarchical cluster analysis (HCA) is an effective method for classifying samples into different groups based on their similarities of chemical variables (Singh et al. 2012; Kalaivanan et al. 2018; Li et al. 2019). The variables grouped into a cluster possess high homogeneity within a cluster and high heterogeneity between clusters. Ward's linkage method with squared Euclidean distance was used for similarity measurement between the water quality variables. R mode HCA generated a dendrogram grouping the variables into two clusters, and the results are presented in Fig. 9. Cluster 1 included K^+, F^-, pH, Mg^{2+}, Cl^-, Na^+, Ca^{2+}, NO_3^-, SO_4^{2-}, TH, and HCO_3^-, indicating the processes of carbonate dissolution, rock weathering, and pollution (Subba Rao and Chaudhary 2019). Cluster 2 included TDS and EC, suggesting the process of water salinity. According to Singh et al. (2012), HCO_3^-, Ca^{2+}, and Mg^{2+} were classified into the same clusters suggesting that carbonate weathering might be the major source of dissolved ions in the groundwater of the study area.

Factor analysis

FA is a widely used multivariate analytical technique (Liu et al. 2003; Barzegar et al. 2017; Nematollahi et al. 2018;

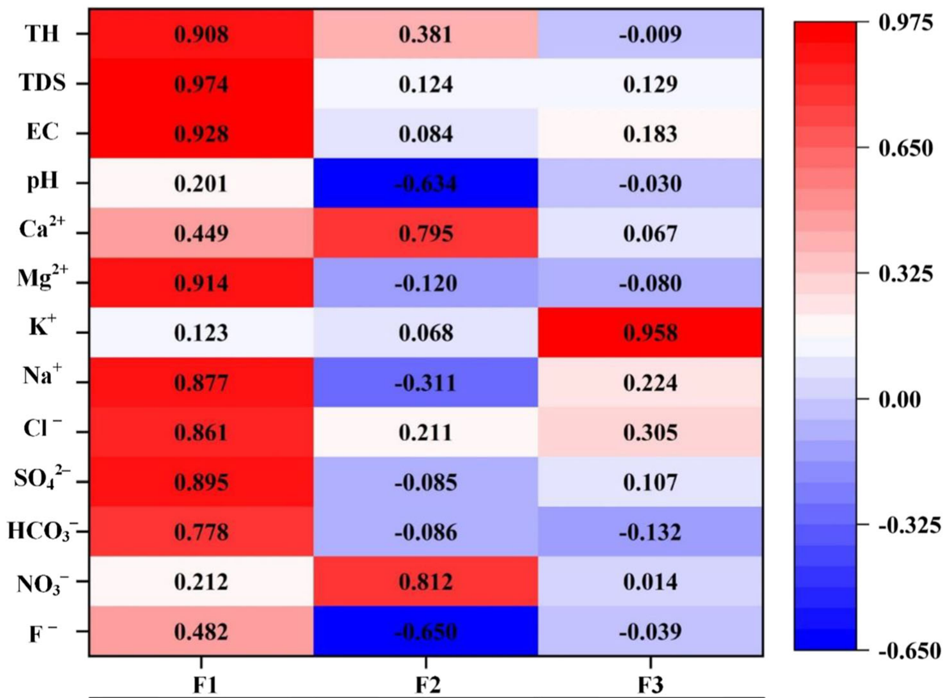
Table 7 Pearson correlation matrix of various chemical constituents in groundwater of the study area

	TH	TDS	EC	pH	Ca^{2+}	Mg^{2+}	K^+	Na^+	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	F^-
TH	1									(a) Phreatic water (n=43)			
TDS	0.962	1											
EC	0.894	0.918	1										
pH				1									
Ca^{2+}	0.617	0.516	0.471		1								
Mg^{2+}	0.827	0.856	0.802			1							
K^+							1						
Na^+	0.806	0.930	0.858			0.865		1					
Cl^-	0.879	0.915	0.870		0.568	0.709	0.395	0.840	1				
SO_4^{2-}	0.829	0.930	0.846		*0.319*	0.827		0.942	0.783	1			
HCO_3^-	0.709	0.649	0.667			0.786		0.604	0.512	0.480	1		
NO_3^-	*0.363*				0.690							1	
F^-	0.458	0.512	0.506	0.416		0.731		0.613	*0.328*	0.536	0.663		1
TH	1									(b) Confined water (n=20)			
TDS		1											
EC		0.941	1										
pH	−0.569			1									
Ca^{2+}	0.842			−0.693	1								
Mg^{2+}	*0.544*					1							
K^+		0.697	0.709				1						
Na^+	*−0.452*	0.644	0.690		*−0.502*		0.776	1					
Cl^-			*0.501*						1				
SO_4^{2-}		0.893	0.795				0.652	*0.539*		1			
HCO_3^-		0.624	0.647				0.609	0.706			1		
NO_3^-	*0.541*			*−0.494*	0.812			*−0.497*				1	
F^-	−0.731			*0.534*	−0.675			0.800				*−0.465*	1

Note: normal and italic values indicate significant correlation at the 0.01 and 0.05 levels (2-tailed), respectively, and values showing insignificant correlation are excluded

Kumar et al. 2020) that reduces the dimensionality of variables and enables the examination of structures in the association between variables. Before using FA to understand the origins of the groundwater samples, the Kaiser-Meyer-Olkin (KMO) statistic and Bartlett's sphericity were performed to evaluate whether the data were suitable for the application of FA. In this study, a KMO value of 0.647 was obtained, which was greater than the threshold value of 0.5, along with Bartlett's sphericity tests of 0, indicating that FA could provide significant results.

Principal component analysis, as a method of FA, was performed using SPSS software by considering eigenvalues greater than 1 and the varimax rotation technique. Kaiser normalization varimax rotation was adopted to obtain a set of loadings with maximum variances of loadings (Kaiser 1958). The FA results, including the factor loading matrix, eigenvalues, and percentages of total and cumulative variances, are presented in Fig. 8, which illustrates that the first three factors with eigenvalues of 6.92, 2.46, and 1.15 explain approximately 81.00% of the total variance. Figure 8 also displays that the variables TH, TDS, EC, Na^+, Mg^{2+}, Cl^-, SO_4^{2-}, and HCO_3^-, whose loadings are shown in red and have strong positive factor loadings in the first factor (F1), account for 53.23% of the total variance. In light of Liu et al. (2003), factor loadings were classified as strong, moderate, or weak based on the corresponding absolute loading values of >0.75, 0.75 to 0.50, and 0.50 to 0.30, respectively. The second factor (F2) explained 18.90% of the total variance and possessed high positive factor loadings for Ca^{2+} and NO_3^-, and the blue color shows moderate negative loadings for pH and F^-. Moreover, 8.87% of the total variance is represented by the third factor (F3), and it is mainly associated with K^+, while other variables had low positive and negative loadings, which may be the result of inputs from domestic activities or the application of fertilizers. Considering the results of the present study area, F1 was designated a natural factor (cation



	F1	F2	F3
Eigenvalue	6.92	2.46	1.15
% of total variance	53.23	18.90	8.87
Cumulative variance (%)	53.23	72.13	81.00

Fig. 8 Heat map of factor loadings

exchange and the weathering and dissolution of minerals) influencing the hydrochemistry of the aquifer. F2 and F3 were associated with anthropogenic pollution and agricultural activity (domestic waste and potassium and nitrogen fertilizers).

The spatial distributions of factor scores were drawn (Fig. 10) to ascertain the influence of processes on specific groundwater areas. Spatial variation maps were produced using the ordinary kriging interpolation technique in GIS. Clearly, most areas showed negative scores on the F1 score map (Fig. 10a), and low positive F1 scores were spread in the northeastern and southern parts. Medium and high positive F1 scores were mainly distributed in Qinyang county and Wenxian county. Medium and high positive F1 scores were observed in samples 11, 26, 29, and 31 and samples 19, 23, and 24, respectively. F1 corresponded to natural processes, and these samples were predominantly used as domestic water. In Fig. 10b, the negative score areas were mainly spread in the southwestern part of the study area, while the medium and high positive F2 scores were located in Anyang and Tangyin counties in the northeastern part of the study area, with shallow water levels (less than 30 m) and many septic tanks and garbage dumps, resulting in a high content of nitrate in the area. Generally, the shallow water samples taken in or near villages had relatively high nitrate contents; in areas far from villages with limited pollution of human life, the nitrate content was lower. For example, samples 37 and 39 in Huixian city and sample 13 in Mengzhou city were from agricultural irrigation wells, which were relatively far from the village and were less affected by anthropogenic pollution and therefore featured relatively low nitrate contents. The high nitrate content in the shallow groundwater in the study area was mainly related to the dry latrines commonly used in rural areas. The poor seepage control conditions of these toilets and the feces of livestock were the main reasons for the high nitrate content in the shallow groundwater. The negative F3 scores were distributed mostly in the northern part and some portions of the southern region (Fig. 10c), whereas the medium positive F3 scores were observed only in the southeastern part, which was mainly affected by unconfined sample 34. The highest F3 scores occurred in sample 34 (6.23), while F3 had a strong positive loading of K^+, and sample 34 had the highest concentration of K^+. There were no high positive scores in the F3 and overall score maps. The overall factor scores were calculated by a weighted factor score, and the weight was the percent of total variance. The distribution pattern of overall scores (Fig. 10d) was similar to that of F1 scores, which suggested that F1 acted as a dominant and widespread controlling factor within the aquifer. The medium positive scores in the overall score map corresponded to the high positive score areas in Fig. 10a. These regions represented the most vulnerable areas of the study area, and this

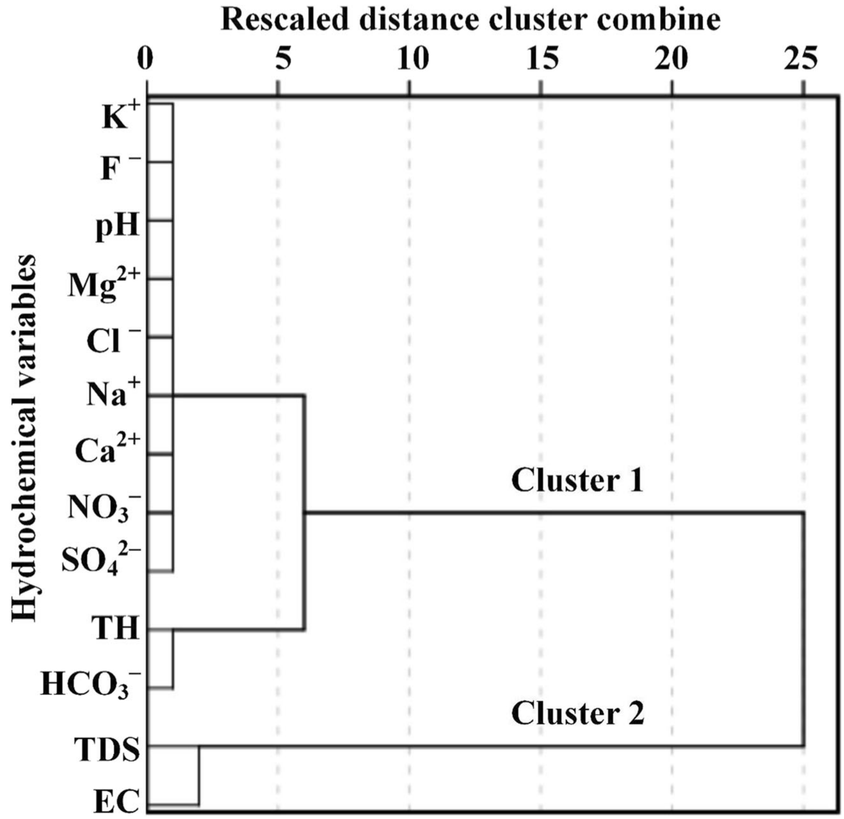


Fig. 9 Dendrogram of R mode cluster showing the cluster of hydrochemical parameters using Ward's linkage

result was consistent with the areas that included the identified highly polluted points (samples 19, 23, and 24) in Fig. 5.

Conclusions

Groundwater is the main source of potable water and irrigation water in the study area. In this study, groundwater quality was examined to evaluate suitability for drinking and irrigation requirements. The following conclusions were drawn from the study area.

The results of the physicochemical analysis of groundwater samples revealed that the groundwater was fresh, hard, and slightly alkaline in nature. The dominance of cations and anions was in the sequence $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ for cations and $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > F^-$ for anions. Based on the Piper diagram and Langelier-Ludwig diagram, most of the samples belonged to the Ca–Mg–HCO_3 type, followed by the Ca–Mg–Cl–SO_4 type hydrochemical facies.

The pH, TDS, Na^+, Cl^-, F^-, and SO_4^{2-} were within the acceptable limits prescribed by the NSDWQ in most of the unconfined samples. For potable use, the parameters that exceeded the standard were TH and NO_3^-, and the exceedance rates were 53.49% and 55.81%, respectively. Moreover, except for one or two samples, almost all confined groundwater samples were within the limits considered acceptable by the NSDWQ. The calculated PIG suggested that the samples were generally suitable for drinking usage because samples with insignificant or low pollution accounted for 93.02% and 100% of the unconfined and confined samples, respectively.

For agricultural groundwater use, the USSL diagram illustrated that most of the groundwater samples belonged to the C2S1 and C3S1 classes, indicating medium to high salinity and a low sodium hazard, rendering the groundwater suitable for irrigation on almost all types of soil. From Wilcox's diagram, except for three unconfined and one confined groundwater samples, all other groundwater samples were plotted in the excellent to good and good to permissible categories for irrigation. The computed results for RSC, PI, and KR revealed high-quality groundwater for irrigation purposes with few exceptions in certain locations, whereas the MR values suggested that 18.60% of unconfined samples and 5% of confined samples were not suitable for agricultural irrigation. Furthermore, the CR index yielded problematic results, with 41.86% of unconfined samples and 20% of confined samples being considered corrosive and unsuitable for irrigation; therefore, noncorrosive pipes are needed to supply water for irrigation purposes.

Correlation analysis, HCA, and FA were performed to identify the relationships among the physicochemical parameters. The results indicated that the influence of natural processes and human activity were important factors controlling the groundwater chemical composition in the

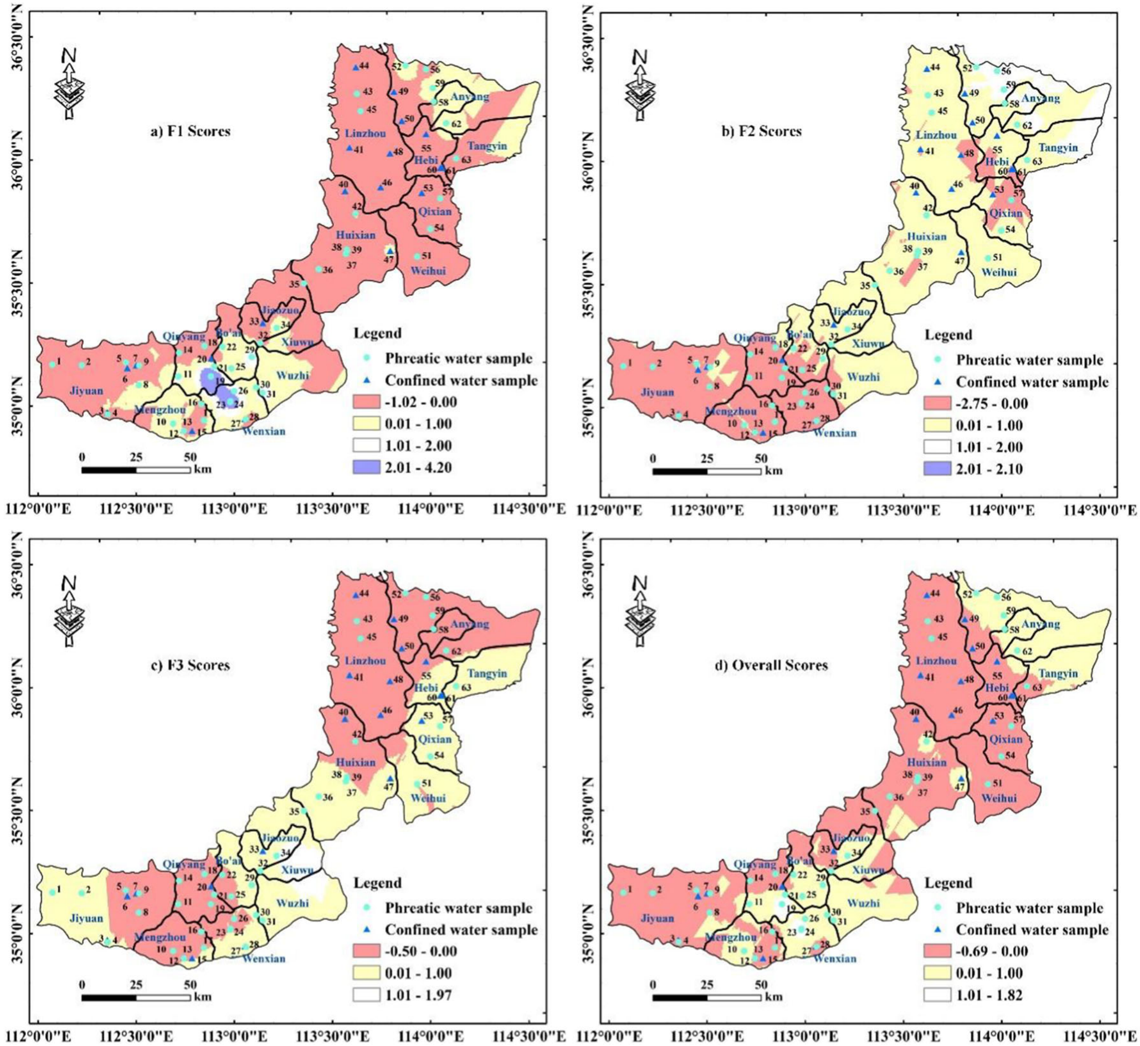


Fig. 10 Distributions of factor scores in the study area

study area. Groundwater samples 19, 23, and 24 had the worst quality in the study area and require appropriate measures to use for drinking and irrigation purposes. The results provide references for the planning, management, and assignment of groundwater supplies for drinking and irrigation in the study area and similar regions around the world.

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Declarations

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