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Hydrochemical processes and groundwater quality assessment in Yushenfu mining area, Northwest China

Ji Liu[a,b,c,*], Min Gao[d], Tiantian Wang[a,b,c,*], Jian Yang[b,c], Qiangmin Wang[b,c]

[a]*China Coal Research Institute, Beijing, 100013, China; email: g73018606@126.com (J. Liu)*
[b]*Xi'an Research Institute of China Coal Technology & Engineering Group Corp, Xi'an, Shaanxi, 710054, China, email: yangjian@cctegxian.com (J. Yang), Wangqiangmin@cctegxian.com (Q. Wang)*
[c]*Key Laboratory of Coal Mine Water Hazard Prevention and Control Technology in Shaanxi Province, Xi'an, Shaanxi, 710054, China, email: wangthpuedu@126.com (T. Wang)*
[d]*Zhongsheng Environmental Technology Development Co, Ltd., Xi'an, Shaanxi, 710065, China, email: gaomin1324@163.com (M. Gao)*

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ABSTRACT

The evolution processes of shallow groundwater in the arid Yushenfu mining area, Shaanxi province, China were explored, and the water quality for drinking and irrigation was assessed. A full understanding of the hydrochemical processes occurring in the study area was obtained through the use of Piper Trilinear and Gibbs diagram and by studying the relationships between the hydrochemical compositions in the groundwater. The results showed that Ca^{2+}, Mg^{2+} and HCO_3^- were the major ions in the groundwater samples, and HCO_3-Ca·(Mg) is the predominant hydrochemical type. The groundwater quality in the study area is currently good due to low concentrations of all the water quality parameters, and it is therefore suitable for drinking and irrigation purposes. Rock weathering, the dissolution of silicate minerals, and cation exchange are the main processes influencing the groundwater chemistry. In addition, excess use of nitrogen fertilizer in nearby agricultural land is responsible for high NO_3^- concentration. However, the impact of mining activities on the groundwater systems is negligible. These results are helpful for better management of water resources in the mining area, and also provide a reference for similar studies in other regions of the world.

Keywords: Hydrochemical processes; Water quality; Groundwater; Yushenfu mining area; Water-rock interaction

1. Introduction

In mining areas, especially in arid to semi-arid regions, groundwater is a crucial resource for domestic, agricultural, and industrial purposes [1,2]. With the revival of the Silk Road economic belt, fresh groundwater is becoming more and more important to northwest China [3]. However, mining activities in this region tend to change groundwater runoff conditions due to discharging a great deal of groundwater, which negatively affects the quality and quantity of groundwater [4]. Therefore, understanding the groundwater quality of mining areas in northwest China is of great urgency for groundwater protection and management [5].

In recent years, a growing realization of the importance of groundwater quality worldwide has seen much research carried out on this topic. A full understanding of hydrochemical characteristics and processes is often needed to identify the water quality of a given source [6]. These factors also offer strong indications of possible changes in water quality [7,8]. For example, Li et al. [5] employed hydro geochemistry techniques to assess the groundwater quality in the Guohua phosphorite mine in southwestern China, and Adimalla [9] collected 194 groundwater samples and used the hydrochemical characteristics to assess the groundwater quality in Telangana State, South India. Other groundwater quality-related studies have been carried out in different locations worldwide [10–14]. In recent

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*Corresponding author.

years, studies have been undertaken [15–17] using hydro geochemical methods on surface and groundwater to identify the effects of mining activities on water circulation and water quality. These studies showed that mining activity has a great influence on the hydrochemical evolution processes and also groundwater quality. Therefore, it is evident that gaining an understanding of the impact of mining activities on the nearby groundwater quality, and providing useful data to help the local government protect water resources, is of key importance.

Yushenfu mining area (located in Yulin city, Shaanxi Province, northwest China) is an important coal production base with abundant high-quality Jurassic coal resources. It is reported that groundwater inrush is a serious threat to safe mining with the increasing exploitation of underground coal [2]; hence, in order to avoid safety accidents, a large amount of groundwater is discharged to the surface. This not only causes wastage of groundwater resources, but also changes the quality of groundwater around the mining areas [6]. It is extremely necessary to understand whether the current mining activities have an impact on the Quaternary shallow aquifer in Yushenfu mining area. Therefore, the present study aims at assessing the quality of groundwater in this area and identifying the dominant hydrochemical processes regulating its chemistry. The results will provide a reference for better management and protection of groundwater resources in the study area.

2. Materials and methods

2.1. Study area

Yushenfu mining area (which includes the Yuheng, Yushen and Shenfu mining areas) is located in Yulin City in the north of Shaanxi Province, China. The study area is situated in the transition zone between the Maowusu desert and the Loess plateau of Northern Shaanxi Province, which is characterized by an arid and semi-arid climate with low rainfall and high evaporation. The average annual precipitation is around 410 mm and the rainy season is from June to September, which accounts for 90% of the annual precipitation. The main recharge source of groundwater in this area is atmospheric rainfall. The average evaporation, on the other hand, is 1712.0 mm—much greater than the rainfall.

According to borehole data, the main strata from oldest to youngest in this area are Jurassic (*J*), Cretaceous (*K*) and Quaternary (*Q*) formations [18], and the Jurassic strata is subdivided into the An'ding (J_{2a}), Zhi'luo (J_{2Z}), and Yan'an (J_{2y}) formations. The Yan'an formation, with buried depth of 300–400 m, is a coal-bearing stratum with 3–7 layers of recoverable coal seams. Quaternary loose aeolian sand with high permeability and hydraulic conductivity is widely distributed throughout the region. The main groundwater types are pore water in loose Quaternary sediments with shallow depth and pore-fissure water in deep Cretaceous formations, which are suitable for domestic, irrigation and industrial uses.

There are three types of landforms: wind-sand, loess, and valley, with the altitude ranging from 800 to 1400 m above mean sea level. Local agricultural lands such as wheat, potato, and corn fields are mainly distributed in wind-sand landforms. The surface water system in this area belongs to the Yellow River system, including the Kuye, Tuwei, and Yuxi, and the Wuding River. In the course of runoff, these surface rivers have a close hydraulic connection with the groundwater. In addition, groundwater is discharged by springs and through leakage into surface rivers under natural conditions.

In the study area, there are a number of large, modern coal mines including Huojitu, Jinjie, Xiaojihan, and Daliuda. The annual output of each coal mine is more than 10 million tons, with the Huojitu coal mine reaching up to 20 million ton/y. A large amount of mine water must be discharged for safe production due to high-intensity mining. In recent years, with the rapid exploitation of coal resources, the groundwater level and surface river runoff have decreased significantly in some local areas, which may affect the quality and quantity of shallow groundwater in the study area.

2.2. Sample collection and analysis

Thirty groundwater samples were collected from wells or springs with good accessibility in the shallow Quaternary loose aeolian sand in the study area, of which 7 samples were collected from drinking water source areas, 6 samples were collected from Yufu mining area (including Yushen and Shenfu mining areas), and the remaining 17 samples were collected from Yuheng mining area. Water samples from drinking water areas are considered to be unaffected by mining activities, since such activities are not allowed in those locations. The exact sampling locations were recorded using a portable GPS (Fig. 1). All groundwater samples were stored in clean 1 L bottles. Prior to sampling, the bottles were washed three times using water from the sampling source. Prior to laboratory testing, all groundwater samples were filtered through a 0.45 μm membrane filter to remove suspended particulates. The groundwater samples were analyzed for pH, electric conductivity (EC), total dissolved solids (TDS), total hardness (TH), and major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, F^-). In addition, trace metals (*Cu, Hg, Cr, Cd, As, Pb, Mn*) and chemical oxygen demand (COD_{cr}) were analyzed to assess the suitability of the groundwater for drinking purposes. The cations and anion concentrations were measured using an ion chromatograph (Thermo Fisher Company, Waltham, USA), and the EC and TDS were measured using an SX751 portable conductivity/pH meter (Shanghai Sanxin Company, Shanghai, China). An EDTA titrimetric method was used for TH analysis and COD_{cr}. Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure trace metals content. The analytical precision was checked by calculating the charge balance error (%CBE) for each sample [19]. The %CBE values of all samples were within ± 5% in this study.

3. Results and discussion

3.1. Hydrochemical characteristics

The results of the physicochemical analysis of the 30 groundwater samples are given in Table 1. The groundwater was found to be alkaline, as its pH ranges from 7.02 to

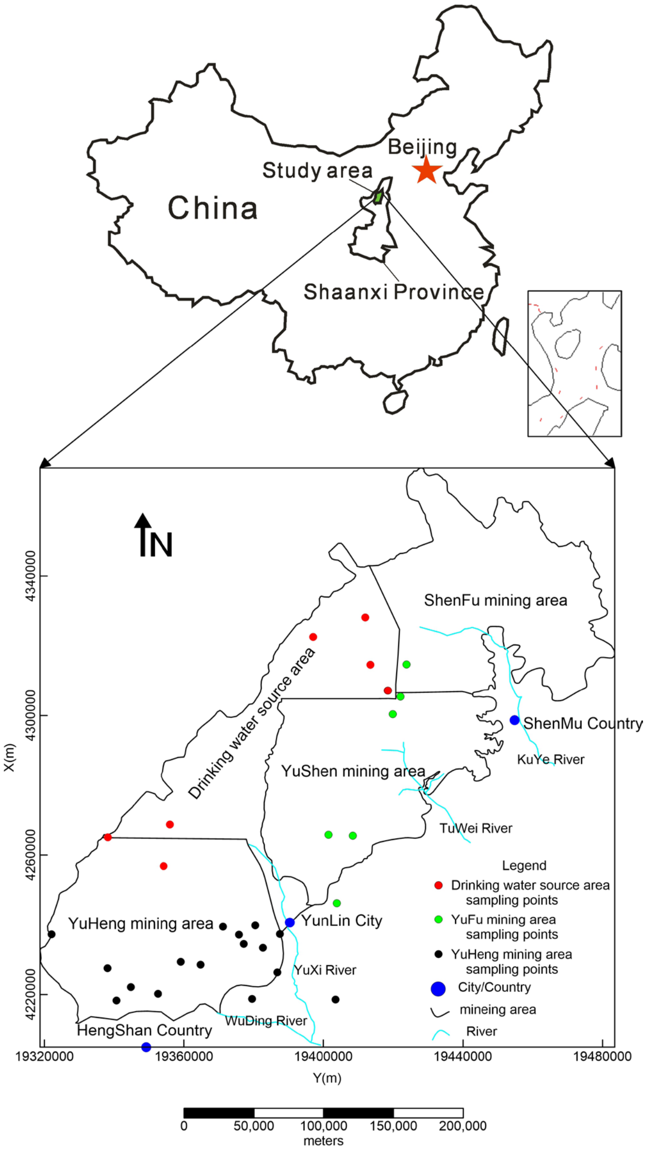

Fig. 1. Map showing groundwater sampling locations.

8.06 (which is almost identical to that of the groundwater in the Ordos Basin, also located in northwestern China [4]). The TDS of the groundwater samples ranged from 185.96 to 395.29 mg/L (with an average of 260.04 mg/L) and from 163.61 to 671.37 mg/L (with an average of 371.29 mg/L) in the drinking water and mining areas, respectively; this demonstrates that the groundwater is fresh water (i.e. TDS < 1000 mg/L), which is suitable for drinking and irrigation purposes according to the Chinese Standard for groundwater quality [20]. The EC of the samples varied from 247.94 to 527.05 μS/cm (with an average of 346.72 μS/cm) and from 218.14 to 895.16 μS/cm (with an average of 423.06 μS/cm) in the drinking water and mining areas, respectively. The TH value measures the dissolved Ca^{2+} and Mg^{2+} expressed as $CaCO_3$; here, the TH of the samples ranged from 130.84 to 260.15 mg/L (with an average of 185.93 mg/L) and from 114.6 to 329.58 mg/L (with an average of 191.69 mg/L) in the drinking water and mining areas, respectively, indicating that the groundwater is soft to slightly hard according to the Chinese Standard for drinking water quality [20]. The TDS, EC, and TH values were higher in the mining areas compared to the drinking water areas; however, in absolute terms, these parameters are low, which may be due to the good runoff conditions of the groundwater.

The average concentrations of the major ions in all sampled areas were basically uniform, except for SO_4^{2-} and NO_3^-. The concentrations of Ca^{2+}, Na^+, Mg^{2+}, SO_4^{2-}, and HCO_3^- are relatively high in the groundwater samples (Fig. 2). The order of cation and anion concentrations was $Ca^{2+} > Na^+ > Mg^{2+} > K^+ > NH_4^+$ and $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > NO_2^-$, respectively. The Ca^{2+}, Mg^{2+}, and HCO_3^- concentrations ranged from 25.01 to 112.3 mg/L (with an average of 55.08 mg/L), 4.72–30.63 mg/L (with an average of 12.83 mg/L), and 138.17–311.81 mg/L (with an average of 210.18 mg/L), respectively. The SO_4^{2-} concentration ranged from 17.27 to 73.82 mg/L (with an average of 35.64 mg/L) and from 5.7 to 299.3 mg/L (with an average of 46.47 mg/L) in the drinking water and mining areas, respectively. The NO_3^- concentration ranged from 0.5 to 26.0 mg/L (with an average of 5.36 mg/L) and from 4.00 to 94.00 mg/L (with an average of 29.17 mg/L) in the drinking water and mining areas, respectively, indicating that nitrate pollution was present in the study area. The NO_2^- and SO_4^{2-} concentrations in all samples were below the acceptable limits for drinking purposes (0.02 mg/L and 250 mg/L, respectively), except for samples G16 and G20.

Overall, the predominant cations Ca^{2+} and Mg^{2+} accounted for 80.9% of the total cationic balance, while the predominant anion HCO_3^- accounted for 75.7% of the total anionic balance. According to the local geological conditions, the dissolution of silicate minerals such as plagioclase and anorthite, and of calcium minerals such as gypsum or anhydrite are responsible for the high concentrations of Ca^{2+}, Mg^{2+}, and HCO_3^-. In addition, the high concentration of NO_3^- is chiefly from fertilizers, which indicates that the anthropogenic impact on the groundwater system in this area cannot be ignored. Low concentrations of Cl^- in groundwater are normally attributed to precipitation [21]. The SO_4^{2-} concentration in the shallow aquifer was also relatively low compared to groundwater from the Yan'an formation [18], which indicates that the impact of mining activities on groundwater systems was negligible.

Piper trilinear diagrams [22] are the most commonly-used tool for determining the type of groundwater based on its hydrochemical characteristics [23,24]. The Piper diagram of the groundwater is shown in Fig. 3. As the figure shows, the samples mostly fall into zone II, demonstrating the dominance of alkaline earths (Ca^{2+}, Mg^{2+}) over alkalis (Na^+, K^+), weak acids (HCO_3^-, CO_3^{2-}) over strong acids (SO_4^{2-}, Cl^-), and a carbonate hardness exceeding 50% [25]. Fig. 3 further indicates that groundwater samples predominantly occur as the HCO_3-Ca·(Mg) type, which indicates that the weathering of silicate minerals is the main process regulating the groundwater chemistry in this area. Furthermore, the types of the groundwater samples collected from the drinking water source areas were the same as those of the remaining samples, indicating that the groundwater quality in this area is predominantly regulated by natural processes and that mining activity has little impact on it.

Table 1
Results of the physicochemical analysis of the collected groundwater samples

Sampling No.	Location	pH	K^+	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+	SO_4^{2-}	Cl^-	HCO_3^-	NO_3^-	NO_2^-	TDS	COD	TH	EC
G1	Drinking water source area	7.88	2.09	8.32	42.41	8.59	0.01	17.27	5.63	175.51	0.50	0.01	191.97	1.16	141.27	255.97
G2		7.59	1.08	38.60	50.44	22.38	0.01	50.09	30.96	265.13	26.00	0.01	371.69	0.80	218.10	495.59
G3		7.70	0.64	10.77	64.60	10.09	0.01	26.23	14.07	233.39	0.50	0.00	258.27	1.32	202.85	344.36
G4		7.80	1.09	40.58	78.36	15.66	0.01	73.82	26.74	289.40	0.50	0.00	395.29	1.28	260.15	527.05
G5		7.87	1.04	15.48	25.01	16.61	0.01	20.91	12.67	166.17	0.50	0.00	185.96	0.88	130.84	247.94
G6		7.80	0.09	0.01	71.68	4.72	0.01	29.55	9.85	182.98	7.50	0.00	229.72	0.80	198.42	306.29
G7		7.84	0.25	0.38	49.13	6.61	0.01	31.60	4.22	147.50	2.00	0.01	187.38	0.76	149.89	249.84
G8	ShenFu mining area	7.76	0.43	3.85	50.62	11.51	0.01	6.52	7.04	179.24	26.50	0.01	216.50	0.76	173.79	288.67
G9		7.44	0.97	16.29	112.30	11.45	0.01	25.50	45.04	222.19	98.00	0.00	439.49	0.84	327.56	585.98
G10		7.93	0.63	5.92	58.45	12.88	0.01	15.69	9.85	216.59	4.00	0.02	239.71	0.64	198.98	319.61
G11	YuShen mining area	7.49	0.64	4.60	87.17	9.26	0.01	48.49	29.56	229.66	10.00	0.01	337.17	1.24	255.79	449.57
G12		7.94	1.91	4.33	29.06	10.21	0.01	5.83	1.41	143.77	15.00	0.01	163.61	0.80	114.60	218.14
G13		7.88	0.12	9.90	26.45	14.24	0.01	5.70	5.63	169.91	6.50	0.00	176.18	0.96	124.68	234.91
G14	YuHeng mining area	7.81	1.04	13.46	40.06	13.51	0.02	13.25	4.22	188.58	28.00	0.01	228.75	0.68	155.66	305.00
G15		7.85	0.09	16.68	32.43	15.98	0.01	9.16	7.04	192.31	25.00	0.01	231.32	0.60	146.78	308.43
G16		7.90	0.76	161.90	31.87	9.12	0.01	299.30	15.48	175.51	36.00	0.01	671.37	0.92	117.13	895.16
G17		7.83	0.40	102.80	27.38	13.81	0.01	169.90	14.07	197.91	7.00	0.00	454.12	0.60	125.23	605.50
G18		7.72	1.11	6.12	37.67	7.18	0.01	12.77	4.22	138.17	22.50	0.01	178.61	0.80	123.63	238.15
G19		7.75	0.53	68.38	34.93	8.57	0.03	88.23	7.04	194.18	33.50	0.00	367.81	0.64	122.51	490.41
G20		7.02	0.12	27.39	99.89	14.12	0.01	47.13	46.45	224.05	97.00	0.12	462.25	1.92	307.57	616.34
G21		7.27	0.11	11.20	109.10	8.80	0.01	22.03	60.52	302.47	7.00	0.01	388.47	0.88	308.66	517.96
G22		7.36	1.08	13.55	56.23	8.02	0.05	21.57	9.85	227.79	15.00	0.01	257.57	1.32	173.43	343.43
G23		7.53	0.58	7.43	48.32	8.38	0.03	10.79	4.22	207.25	11.00	0.00	213.55	1.32	155.16	284.73
G24		7.75	0.32	6.42	38.91	10.72	0.01	15.81	4.22	166.17	25.00	0.01	203.53	0.92	141.30	271.37
G25		7.64	0.44	4.46	56.01	9.23	0.01	14.92	5.63	182.98	38.00	0.00	240.43	0.76	177.86	320.57
G26		7.49	1.12	8.85	49.64	22.80	0.01	33.79	5.63	240.86	25.00	0.01	287.65	0.92	217.83	383.53
G27		7.39	0.92	16.56	81.48	30.63	0.01	47.96	12.67	278.20	83.00	0.00	430.43	1.00	329.58	573.91
G28		7.49	0.67	30.04	90.59	19.21	0.01	39.61	57.71	274.47	37.00	0.01	434.47	0.84	305.30	579.30
G29		7.92	0.35	24.80	44.31	9.86	0.01	45.72	5.63	181.11	11.00	0.00	249.58	0.92	151.24	332.78
G30		8.06	0.07	94.06	27.78	20.69	0.01	69.18	26.74	311.81	10.00	0.01	425.17	0.84	154.56	566.89

Unit: mg/L except pH and EC (μS/cm)

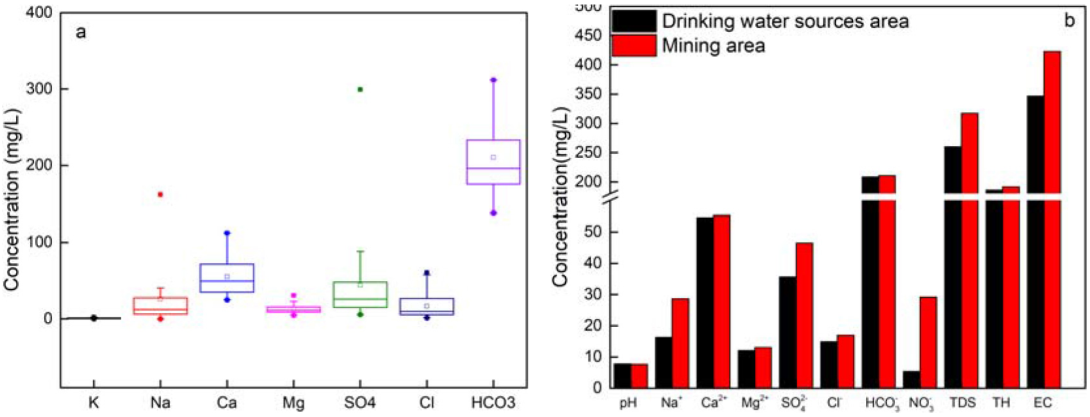

Fig. 2. (a) Box chart and (b) histogram of predominant ion concentrations in the groundwater samples.

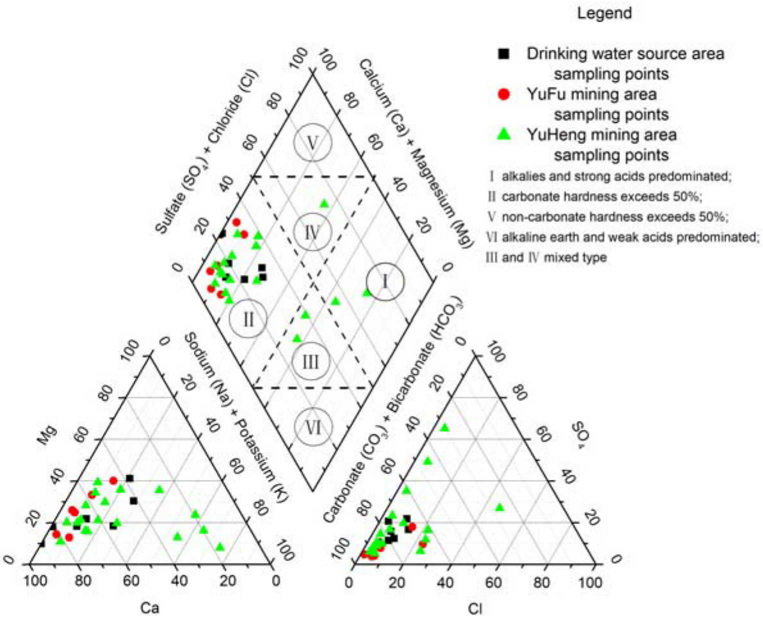

Fig. 3. Piper trilinear diagram of the groundwater samples.

3.2. Processes influencing groundwater chemistry

3.2.1. Water-rock interaction

Here, the natural processes regulating groundwater chemistry in the study area are discussed. The Gibbs diagram [26] is a powerful tool for determining the mechanisms controlling surface water evolution. In recent years, it has been utilized to explore the groundwater evolution processes in various locations in northwestern China [2,27]. The mechanisms illustrated in a typical Gibbs diagram include evaporation-crystallization processes, rock weathering dominance, and precipitation dominance. In the present study, the diagram was applied to understand the processes regulating the groundwater chemistry (Fig. 4a). As the figure illustrates, all of the groundwater samples fall into the rock weathering zone, which suggests that rock weathering is the major process regulating the water chemistry of shallow groundwater in the study area. The Mg^{2+}/Ca^{2+} and Mg^{2+}/Na^{+} ratios can also be used to monitor the processes of rock interaction and soil salt leaching [28]. Here, the presence of a low Mg^{2+}/Ca^{2+} ratio and a high Mg^{2+}/Na^{+} ratio (Fig. 4b) indicates that rock interactions and the leaching of calcium salts are the main factors governing the groundwater chemistry.

Generally, there are three processes contributing to groundwater chemical compositions: dissolution of evaporates, dissolution of carbonates, and silicate weathering [29]. The Na/Ca vs. HCO_3 and Na/Ca vs. Mg diagrams (Figs. 4c and 4d) demonstrate that the groundwater is not only influenced by silicate weathering but is also affected by carbonate dissolution [29,30]. However, the relationship between (Ca + Mg) and HCO_3 (Fig. 5c) indicates that most of the water samples are close to the 1:1 line, which suggests the dominance of silicate weathering [Eq. (1)]. In addition, the values of $\sum$ Cation/(Cl+SO_4) (where $\sum$ Cation (m Eq/L) = Ca + Mg + Na + K – Cl) in most groundwater samples are approximately equal to 1, indicating that the dissolution of silicate minerals (especially plagioclase) occurs in the shal-

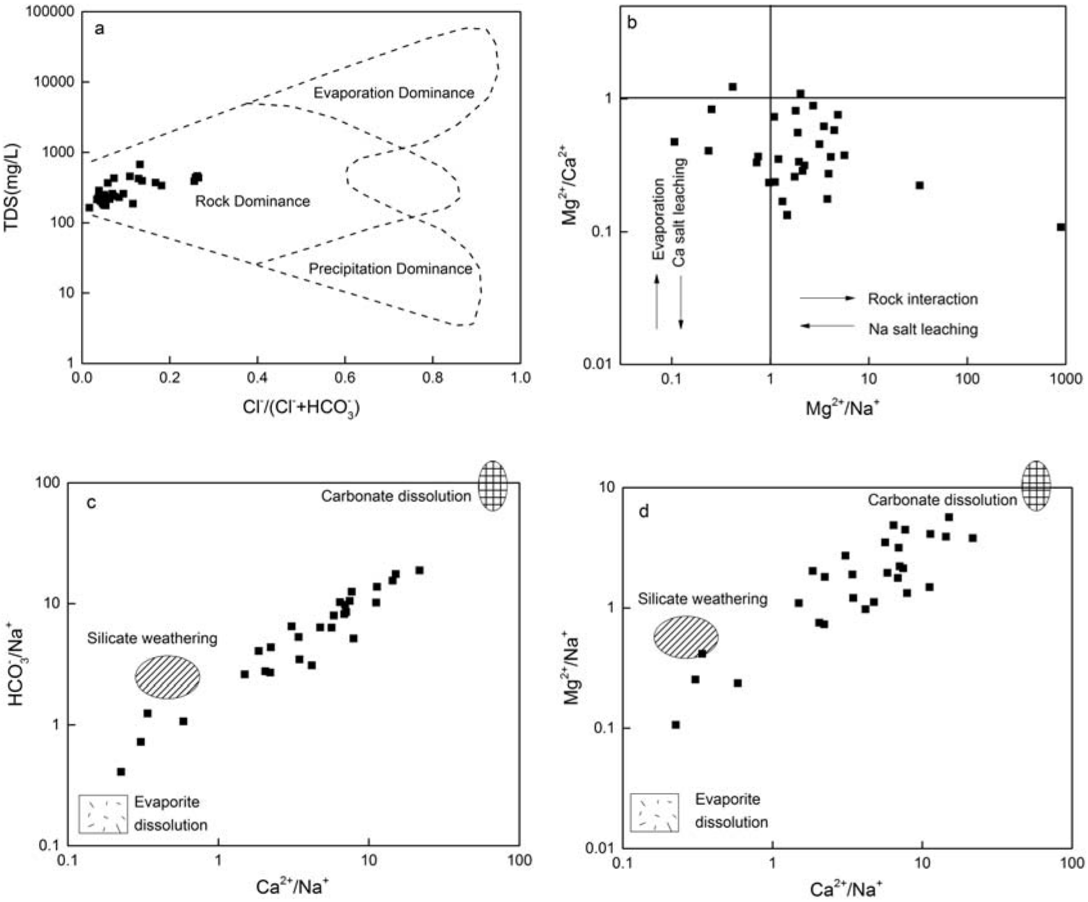

Fig. 4. Plots of (a) Gibbs diagram, (b) Mg/Na vs. Mg/Na, (c) Ca/Na vs. HCO_3/Na, and (d) Ca/Na vs. Mg/Na.

low groundwater [Eq. (2)] and that human activities have little influence on the groundwater quality [2,31].

The relationship between Cl^- and other ions has been widely used to study water-rock interactions since Cl^- is basically not involved in hydrogeochemical reactions in aquifers [32,33]. Theoretically, the value of Na/Cl is equal to 1 if the main source of Na is the dissolution of halites. In the present study, the high value of Na/Cl above 1 indicates a contribution from either the weathering of Na-containing silicate minerals (Fig. 5a) or cation exchange between Ca and Na [34]. When the dissolution of calcite, dolomite, and gypsum are the dominant reactions in the groundwater system, the ratio of (HCO_3^- + SO_4^{2-}) to (Ca^{2+} + Mg^{2+}) will be close to the theoretical 1:1 line [35]. Fig. 5d illustrates that the majority of the groundwater samples fall below this line. The excess of (HCO_3^- + SO_4^{2-}) over (Ca^{2+} + Mg^{2+}) suggests that the alkalis (Na^+ + K^+) are needed to balance the excess (HCO_3^- + SO_4^{2-}) [36]. This may be further evidenced by the fact that the media of the shallow aquifer are fine-to-medium sand, wherein silicates are the dominant minerals.

$$2CaAl_2Si_2O_8 + 4CO_2 + 6H_2O \rightleftharpoons 2Al_2Si_2O_5(OH)_4 + 2Ca^{2+} + 4HCO_3^- \tag{1}$$

$$2CaAl_2Si_2O_8\cdot 2NaAlSi_3O_8 + 6CO_2 + 9H_2O \rightleftharpoons 3Al_2Si_2O_5(OH)_4 + 2Ca^{2+} + 2Na^+ + 6HCO_3^- + 4SiO_2 \tag{2}$$

3.2.2. Cation exchange

Another important process for controlling the chemical constituents in groundwater is cation exchange [28,37]. To study the occurrence of cation exchange, Schoeller [38] proposed two chloro-alkaline indices: CAI-1 and CAI-2, which are calculated as follows:

$$\text{CAI-1} = \frac{Cl^- - \left(Na^+ + K^+\right)}{Cl^-} \tag{3}$$

$$\text{CAI-2} = \frac{Cl^- - \left(Na^+ + K^+\right)}{HCO_3^- + SO_4^{2-} + CO_3^{2-} + NO_3^-} \tag{4}$$

The two indices will both be positive if an exchange between Na^+ in the groundwater and Ca^{2+}/Mg^{2+} in the aquifer materials occurs, as expressed in Eq. (5), whereas negative values indicate reverse cation exchange, as expressed in Eq. (6). As shown in Fig. 6a, the CAI-1 and CAI-2 values of most of the groundwater samples were negative indicating that reverse cation exchange occurs in the most of the study area and that cation exchange exists in some locations, which is consistent with the previous discussion.

$$2Na^+ + (Ca,Mg)X_2 \rightleftharpoons (Ca,Mg)^{2+} + 2NaX \tag{5}$$

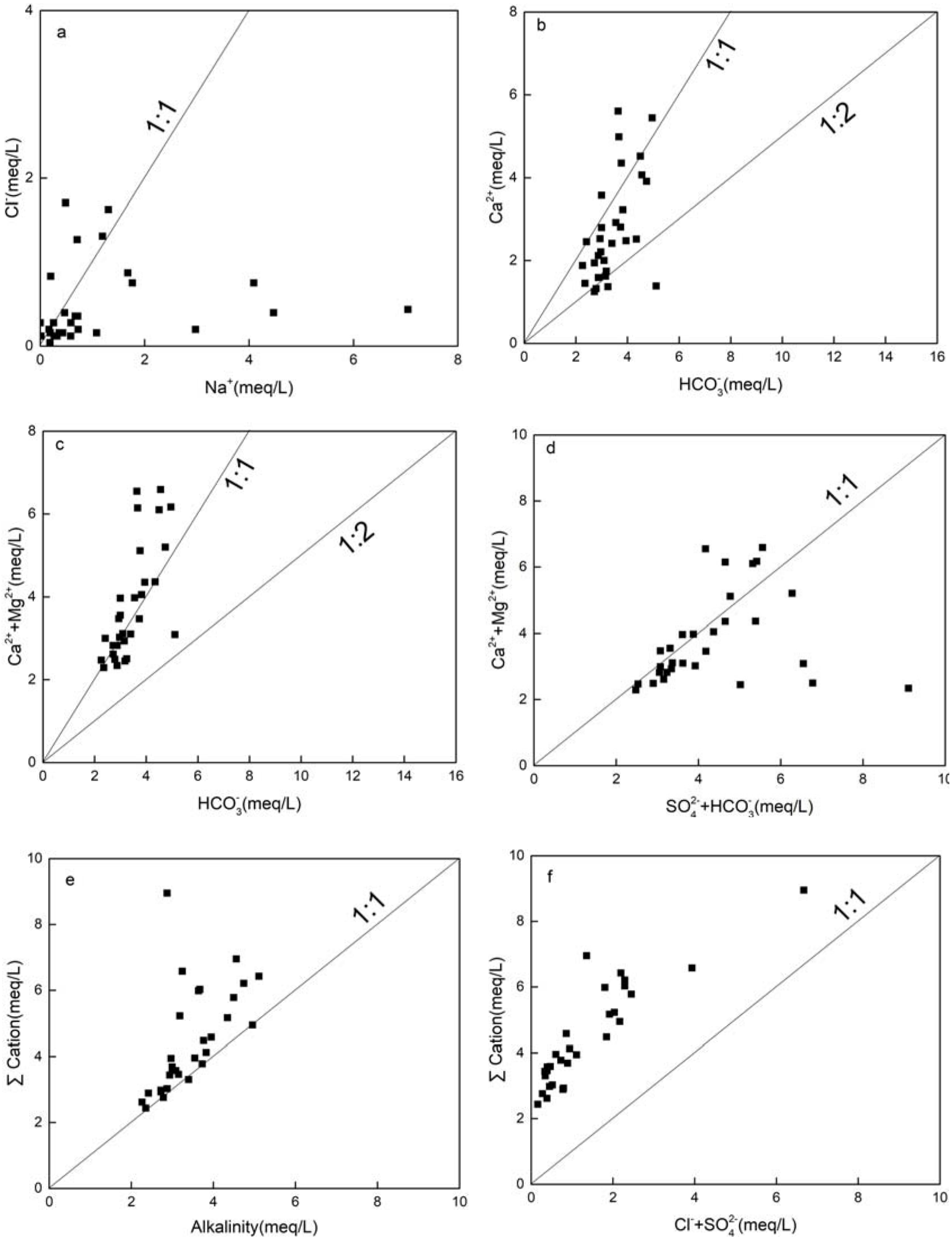

Fig. 5. Relationships between hydrochemical species in the groundwater: (a) Na^+ vs. Cl^-, (b) HCO_3^- vs. Ca^{2+}, (c) HCO_3^- vs. (Ca^{2+}+ Mg^{2+}), (d) (SO_4^{2-}+ HCO_3^-) vs. (Ca^{2+} + Mg^{2+}), (e) Alkalinity vs. ∑Cation, f (Cl^- + SO_4^{2-}) vs. ∑Cation.

$$(Ca,Mg)^{2+} + 2NaX \rightleftharpoons 2Na^+ + (Ca,Mg)X_2 \qquad (6)$$

Furthermore, when cation exchange occurs, the relationship between (Na^+ + K^+ − Cl^-) and [(Ca^{2+} + Mg^{2+}) − (HCO_3^- + SO_4^{2-})] should be linear with a slope of −1 [39]. Figure 6b shows that this relationship can be fitted as a straight line with a slope of −1.0595 and a y-intercept of +0.1587, with a correlation coefficient of 0.91, which indicates the occurrence of cation exchange in the study area.

3.2.3. Anthropogenic activities

The influence of mining activities on shallow groundwater quality is mainly through the drainage of mine water into shallow aquifers or through lowing the water level of

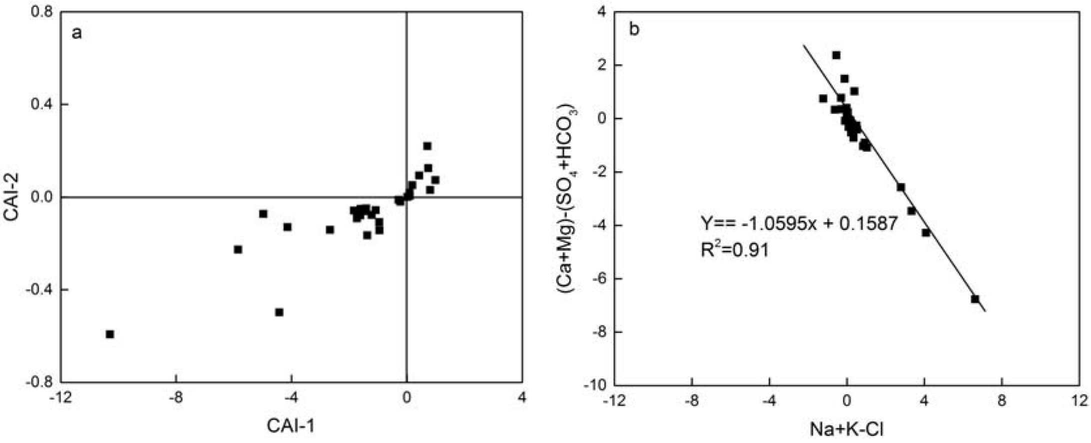

Fig. 6. Plots of (a) CAI-1 vs. CAI-2 and (b) [(Ca + Mg) – (SO_4 + HCO_3)] vs. (Na + K – Cl).

said aquifers. SO_4^{2-} in groundwater is commonly derived from gypsum ($CaSO_4\cdot 2H_2O$) and anhydrite ($CaSO_4$) and its concentration in the mine water is higher compared to that in the Quaternary shallow aquifer. In the Guojiawan coal mine, which is located in the Yufu mining area, the average SO_4^{2-} concentration of mine water is above 200 mg/L with a maximum of 548 mg/L [40]. However, in the Quaternary shallow aquifer, the SO_4^{2-} concentrations were below 100 mg/L except for G16 and G17 (Fig. 7a). HCO_3^- in groundwater is commonly derived from the dissolution of silicate minerals, which tend to increase as the shallow groundwater level decreases. Nevertheless, in the present study, the HCO_3^- concentration in the mining areas was basically the same as that in the drinking water areas where the groundwater was not affected by mining activities. Thus, the mining activities seemingly have little effect on groundwater quality in the Quaternary aquifer, as the SO_4^{2-} concentrations therein became low due to both the dilution of the aquifer with abundant water and good runoff conditions following the discharge of mine water.

The chief sources of NO_3^- and Cl^- are fertilizers and municipal or domestic sewage discharge [41]. The concentrations of these ions are usually affected mainly by irrigation and industrial activities; therefore, high concentrations of NO_3^- and Cl^- can represent that shallow groundwater is affected by irrigation and industrial activities. The relationships among NO_3^-, and Cl^- concentrations in the study area samples are shown in Fig. 7b. It can be observed that the number of groundwater samples with NO_3^- concentrations exceeding the allowable Chinese limit (20 mg/L) in mining areas is larger than those in drinking water areas, whereas the concentrations of Cl^- did not exceed the WHO limits (250 mg/L) in any of the samples. These results indicate that the groundwater chemistry has been affected by irrigation. There are many agricultural lands widely distributed within the study area; in these areas, fertilizers, particularly nitrogen-based ones are used, resulting in nitrogen being released into the soil and consequently increasing the NO_3^- levels in the groundwater samples [Eqs. (7) and (8)]. These results are consistent with Wang et al. study [42]. In summary, industrial pollution and mining activities have a limited impact, but irrigation has greater impact on groundwater quality.

$$2NH_4^+ + 3O_2 \rightleftharpoons 2NO_2^- + 4H^+ + 2H_2O \tag{7}$$

$$2NO_2^- + O_2 \rightleftharpoons 2NO_3^- \tag{8}$$

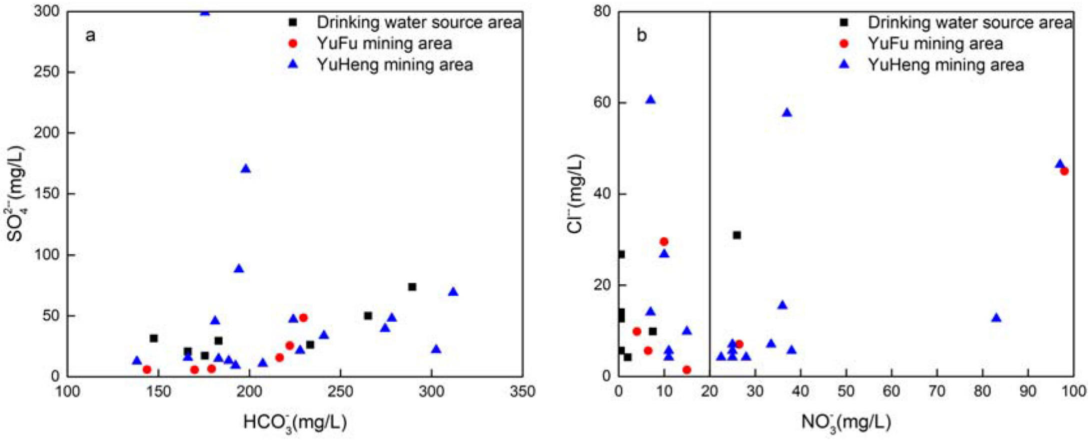

Fig. 7. Plots of (a) HCO_3^- vs. SO_4^{2-} and (b) NO_3^- vs. Cl^-.

3.3. Water quality assessment

Groundwater samples in the study area were compared with the Chinese Standard for drinking water quality [20] and the WHO guidelines for drinking water quality [43]. The pH of the groundwater ranged from 7.02 to 8.06, within the desirable limits for drinking (6.5–8.5). The permissible limits of TDS and TH are 1000 and 450 mg/L, respectively, based on the Chinese guidelines. Here, the TH and TDS in all groundwater samples were both found to be below the permissible limits for drinking. The concentrations of all major ions were within their corresponding permissible limits according to the Chinese standard—except for NO_3^-, the concentration of which ranged from 0.5 to 98.0 mg/L (with an average of 23.62 mg/L), and was in between the permissible limits set the Chinese guidelines (20 mg/L) and those recommended by the WHO [43] (50 mg/L) for almost all the samples. The concentrations of trace metals and COD_{cr} of the samples were all very low and were well within the permissible limits recommended by the WHO [43]. Overall, these results confirm that the groundwater in the study area is suitable for drinking purposes at present.

Groundwater for irrigation purposes should satisfy the demands of soil and plants for good growth and high crop production. Electrical conductivity (EC) and Na content (Na%) play an important role in classifying water for irrigation purposes [40]. Irrigation water with a high salt content not only directly affects plant growth, but also indirectly affects plant growth by increasing the osmotic pressure of the soil solution, thus affecting the structure, permeability, and aeration of the soil [25]. EC in irrigation water is positively correlated with TDS and can indicate the total concentration of soluble salts. It may be classified into four categories (C1–C4): low (EC ≤ 250 µS/cm), medium (within the range of 250–750 µS/cm), high (within the range of 750–2250 µS/cm), and very high (within the range of 2250–5000 µS/cm) [25]. Irrigation water a high EC value can make the soil saline.

The sodium adsorption ratio (SAR) is calculated using the formula:

$$\mathrm{SAR} = \frac{\mathrm{Na}^+}{\sqrt{\frac{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}}{2}}} \tag{9}$$

Irrigation water is divided into four categories (S1–S4) on the basis of SAR: low (0–10), medium (10–18), high (18–26), and very high (> 26) [25]. If irrigation water has a high Na and a low Ca concentration, the cation-exchange complex saturated with Na can destroy the soil structure through the dispersion of clay particles [40].

Percent Na (Na%) is also widely utilized for assessing the suitability of groundwater quality for irrigation (Wilcox 1955), and is calculated according to the formula:

$$\mathrm{Na\%} = \frac{\mathrm{Na}^+ + \mathrm{K}^+ \times 100}{\left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^+ + \mathrm{K}^+\right)} \tag{10}$$

The quantity of bicarbonate and carbonate ions (HCO_3^- and CO_3^{2-}) in excess of alkaline earths (Ca^{2+} and Mg^{2+}) also affects the suitability of water for irrigation. The effects of carbonate and bicarbonate can be quantified using Residual Sodium Carbonate (RSC), which is calculated according to:

$$\mathrm{RSC} = \mathrm{HCO}_3^- + \mathrm{CO}_3^{2-} - \left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right) \tag{11}$$

Water quality classification standards for irrigation purposes, based on SAR, EC, Na%, and RSC are given in Table 2.

In the present study, the calculated RSC value was less than 2.0 meq/L for all samples, indicating that the groundwater is suitable for irrigation use. The EC ranged from 218.14 to 895.16 µS/cm in the study area, which is in the low-to-medium range. The max SAR of the samples was 6.5. Plotting the data on a US salinity diagram [44] (Fig. 8a) shows that all groundwater samples fall into zones C1S1 and C2S1, except for one sample which falls within zone C3S1. The Na% of all groundwater samples varied from 0.07% to 75.1%. As shown in the Wilcox diagram (Fig. 8b), the groundwater samples fall within the excellent to good quality zones except for one sample. Overall, these results demonstrate that the groundwater in the study area is suitable for irrigation purposes.

In the shallow aquifer of the study area, the hydraulic conductivity and permeability are high, and the water yield is strong, indicating good drainage. In addition, the locations of the groundwater samples are mainly close to the rivers, and the shallow groundwater is recharged by atmospheric precipitation and discharged into nearby rivers over a very short time period. Thus, the groundwater in these areas has a much higher renewal rate.

3.4. Groundwater management

It can be seen that the groundwater quality in the study area is mainly affected by irrigation and is slightly affected by industrial and mining activities from the research in the preceding chapters. However, groundwater quality may deteriorate due to the cumulative impacts of increasing mining and industrial activities. Some wise groundwater management measures should be taken by local government. For example, groundwater monitoring network in mining, industrial and irrigation areas must be constructed

Table 2
Water quality classification standards for irrigation purpose

SAR	EC	Irrigation water quality	Na%	RSC	Irrigation water quality
<10	250	Excellent quality	<30	<1.25	Suitable
10–18	250–750	Good quality	30–60	1.25–2.5	Marginally suitable
18–26	750–2250	Acceptable quality	>60	>2.5	Unsuitable
>26	>2250	Unacceptable quality			

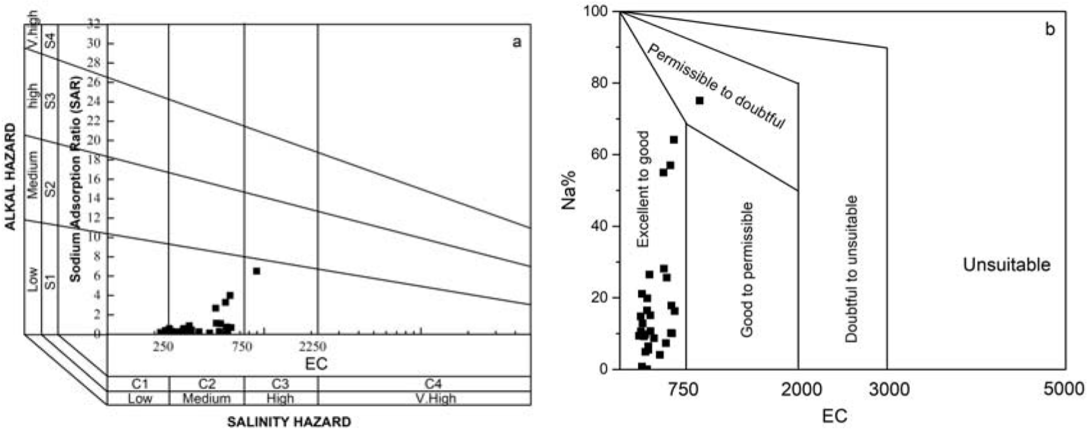

Fig. 8. Diagram of (a) USSL and (b) Wilcox.

to understand the groundwater quality in real-time. And wastewater must be treated before it can be discharged in mining and industrial areas. In addition, scientific support for fertilizers that can be quickly absorbed by plants needs to be strengthened.

4. Conclusions

The conclusions drawn from this study can be summarized as follows:

1. Groundwater in the study area is alkaline, and ranges between fresh and soft water to slightly hard water. The predominant ions are Ca^{2+}, Mg^{2+}, and HCO_3^-. The dominant hydrochemical type in this area is the HCO_3-Ca·(Mg) type. All major ions concentrations are relatively low due to the good runoff conditions.
2. Detailed data analysis shows that natural processes such as rock weathering, the dissolution of silicates, and cation exchange are the main processes controlling the chemical constituents of the groundwater in the study area. In addition, the high NO_3^- concentration indicates that the groundwater is affected by excessive use of nitrogen fertilizer in agricultural areas nearby. However, the low SO_4^{2-} and Cl^- concentrations demonstrate that industrial pollution and mining activities have little impact on the groundwater chemistry.
3. The values of all groundwater quality parameters were below the permissible limits set by the Chinese government and the WHO for drinking purposes, and the calculated SAR, Na% and RSC values were low, indicating that the groundwater in this area is suitable for drinking and irrigation purposes due to the good hydrogeological conditions.

The results of this study have great significance for groundwater management in the study area. Although groundwater in this area is of good quality at present, its quality should be monitored in real-time as mining activities are likely to become more and more intense in the future, likely resulting in negative consequences for the groundwater quality.

Acknowledgements

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