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# Hydrogeochemical Characterization and Quality Assessment of Groundwater in a Long-Term Reclaimed Water Irrigation Area, North China Plain

Xiaomin Gu <sup>1</sup>, Yong Xiao <sup>2,\*</sup>, Shiyang Yin <sup>3,\*</sup>, Qichen Hao <sup>4</sup>, Honglu Liu <sup>5</sup>,  
Zhongyong Hao <sup>5</sup>, Geping Meng <sup>6</sup>, Qiuming Pei <sup>2</sup> and Huijun Yan <sup>7</sup>

<sup>1</sup> School of Geographic Science, Nantong University, Nantong 226000, China; ntugxm@ntu.edu.cn

<sup>2</sup> Faculty of Geosciences and Environmental Engineering, Southwest Jiaotong University, Chengdu 611756, China; pqm@swjtu.edu.cn

<sup>3</sup> School of Renewable Energy, North China Electric Power University, Beijing 102206, China

<sup>4</sup> Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Science, Shijiazhuang 050061, China; haoqichen@mail.cgs.gov.cn

<sup>5</sup> Beijing Water Science and Technology Institute, Beijing 100044, China; liuhonglu@yeah.net (H.L.); haozhongyong2002@163.com (Z.H.)

<sup>6</sup> Beijing Daxing Water Resources Bureau, Beijing 102600, China; mgpmbx@aliyun.com

<sup>7</sup> Geological Environmental Monitoring Central Station of Qinghai Province, Xining 810008, China; yanhj1214@aliyun.com

\* Correspondence: xiaoyong@swjtu.edu.cn (Y.X.); yinshiyang1984@163.com (S.Y.);  
Tel.: +86-180-1000-8002 (Y.X.); +86-010-5150-3095 (S.Y.)

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**Abstract:** Water scarcity has led to wide use of reclaimed water for irrigation worldwide, which may threaten groundwater quality. To understand the status of groundwater in the reclaimed water irrigation area in Beijing, 87 samples from both shallow and deep aquifers were collected to determine the factors affecting groundwater chemistry and to assess groundwater quality for drinking and irrigation purposes. The results show that groundwater in both shallow and deep aquifers in the study area is weakly alkaline freshwater with hydrogeochemical faces dominated by  $\text{HCO}_3\text{-Na}\cdot\text{Mg}\cdot\text{Ca}$ ,  $\text{HCO}_3\text{-Mg}\cdot\text{Ca}\cdot\text{Na}$ ,  $\text{HCO}_3\text{-Ca}\cdot\text{Na}$ , and  $\text{HCO}_3\text{-Na}$ . The chemical composition of groundwater in both shallow and deep aquifers is dominantly controlled by the dissolution of halite, gypsum, anhydrite, and silicates weathering, as well as ion exchange. Geogenic processes (rock weathering and ion exchange) are the only mechanisms controlling groundwater chemistry in deep aquifers. Besides geogenic processes, evaporation and anthropogenic activities also affect the chemistry of shallow groundwater. Quality assessment reveals that both shallow and deep groundwater are generally suitable for drinking and irrigation purposes. The quality of deep groundwater is more excellent for drinking than shallow groundwater. However, long-term use of deep groundwater for irrigation exhibits higher potential risks to deteriorate soil property due to the relative higher permeability indexes (PI). Therefore, it is recommended that deep groundwater is preferentially used for drinking and domestic purpose, and shallow groundwater for agricultural irrigation.

**Keywords:** hydrochemistry; influencing factors; groundwater quality assessment; EWQI; Beijing

## 1. Introduction

Water scarcity has been one of the most serious problems that restrict economic development in many regions around the world, especially in arid and semiarid regions [1,2]. Due to the spatio-temporal availability and easy accessibility, groundwater becomes the major source of freshwater

for agricultural, domestic, and industrial purposes [3,4]. These purposes are dominantly controlled by groundwater chemistry [5]. Therefore, comprehending the characterization of groundwater chemistry and its controlling factors is vital for preservation and proper management of these precious resources, as well as realizing sustainable use of groundwater [6,7].

As one of the water shortage megacities in the world, Beijing relies heavily upon groundwater resources for its various usages, over 60% of annual total water supply quantity is groundwater [3]. Due to long-term overexploitation, groundwater level has declined sharply during the past decades [8]. In order to alleviate the water shortage, wastewater and reclaimed water have been utilized for agricultural irrigation in Beijing Plain since the 1950s [9]. Water reuse for irrigation may lead to some negative environmental consequences, such as soil structure deterioration, enrichment of heavy metals and other pollutants in soils and agricultural corps, groundwater pollution as well [9,10]. Numerous researches have been conducted to get insight into these consequences, but most of them concentrated on the effects on soil and plant [11–15]. Only a few researches were concerned on the influences of this reuse on groundwater [9,16–18]. For example, Bao et al. found that long-term wastewater irrigation had resulted in nutrient elements and heavy metals accumulation in soil at some extent, but it did not constitute pollution in shallow groundwater [16,19]. Wang et al. reported that nonylphenol, a kind of organic pollutant from wastewater, had been found existing in groundwater, and its distribution and concentration in groundwater were related to the measure of wastewater irrigation and groundwater depth [18]. Niu et al. applied geostatistics to determine the spatial variation of groundwater quality in a reclaimed water irrigation area in Beijing, and found that reclaimed water irrigation was not the major factor influencing groundwater quality [17]. However, the hydrogeochemical characterization and quality of groundwater in wastewater and reclaimed water irrigation areas are still not well known. This may limit the protection and proper utilization of groundwater resources in Beijing, especially in reclaimed water irrigation areas.

The aims of this study are (1) to address the hydrochemical characterization of groundwater in Beijing's reclaimed water irrigation area, (2) to identify the factors influencing the chemical composition of groundwater, and (3) to assess the suitability of groundwater quality for drinking and agricultural irrigation purposes. This work will be helpful in the protection and management of groundwater in Beijing, and be useful for groundwater resources management in another part of the world facing the similar situation.

## 2. Materials and Methods

### 2.1. Study Area

The study area is located in the southeastern part of the Beijing plain with longitudes of 116°32'–116°43' E and latitudes of 39°26'–40°02' N. It covers an area of about 373 km<sup>2</sup> (Figure 1). It is characterized by a temperate continental monsoon climate. The average annual rainfall in the study area is 554.5 mm, with approximate 70% occurred from June to September. While the annual potential evaporation rate is 1800 mm, which is about three times of the annual precipitation.

As shown in the Figure 2, the terrain of this area is flat, with a slight gradual slope from northwest to southeast. The study area is located in the downstream area of Yongding River and Chaobai River watershed and formed by their alluvial sediments. The Quaternary deposits distribute widely and the thickness gradually increases from northwest to southeast with a maximum thickness of 300 m. The strata present an alternating lithologic structure of middle-fine sand and clay. A continuous clay layer is found at a depth of 80 m, above and below which are defined as the shallow aquifer and deep aquifer, respectively [16]. Groundwater is loose-rock pore water occurring in the Quaternary aquifers and flows from northwest to southeast regionally. The water level depth of shallow aquifer ranges from 4 to 9 m, and that of deep aquifer varies from 17 to 21 m (Figure 2). The main components of groundwater recharge include lateral inflow, precipitation infiltration, river and canal leakage, and irrigation infiltration, while the major discharge patterns are artificial abstraction, evaporation, and lateral outflow.

Located in the southeast suburb of Beijing, a large area of farmland was distributed in the study area. Due to lack of water resource, urban sewage was used for agricultural irrigation in the study area since 1969, leading to a sewage irrigation history of over 30 years [9]. Since 2003, reclaimed water from Gaobeidian, Xiaohongmen, and Huangcun wastewater treatment plants (Figure 1) has gradually replaced wastewater and became the major water resource for irrigation in the study area [14,18].

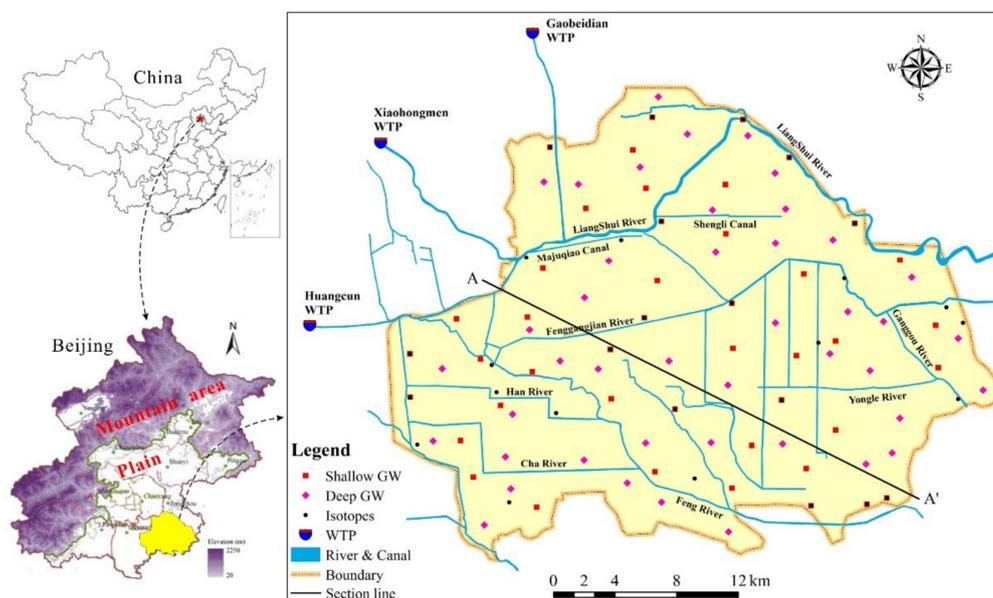


Figure 1. Location of the study area and sampling sites.

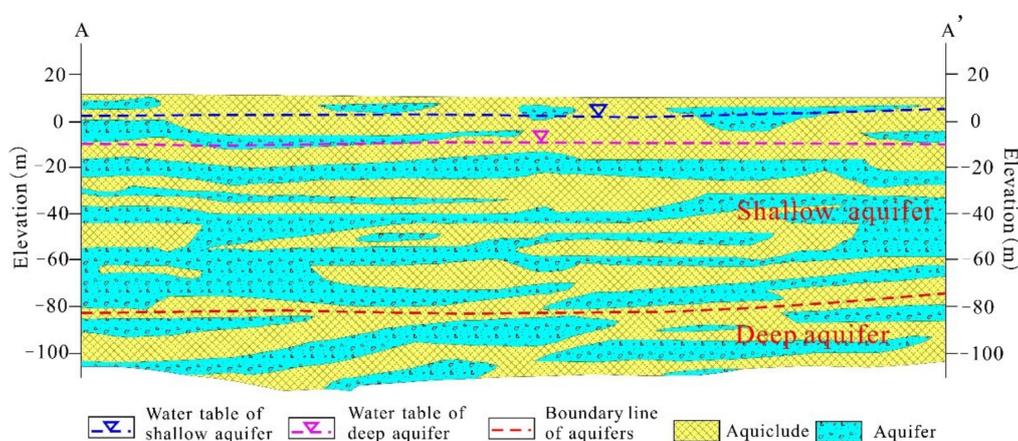


Figure 2. Hydrogeological cross section of the study area.

## 2.2. Sample Collection and Analysis

For this study, 87 groundwater samples, including 44 samples from shallow aquifer and 43 samples from deep aquifer (Figure 1), were collected from boreholes in October 2016 for physiochemical analysis. Prior to sampling, all of the boreholes were pumped for fifteen minutes to remove the stagnant water. Samples were collected in 2.5 L plastic bottles that had been thoroughly pre-cleaned while using the water to be sampled. Temperature (T), hydrogen ion activity (pH), electrical conductance (EC), and total dissolved solids (TDS) were measured in the field while using a multi-parameter device (Multi 350i/SET). The other analyzed indices including major ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^+$ ,  $\text{Mg}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ), nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), and ammonia ( $\text{NH}_4^+$ ) were measured at the Laboratory of Groundwater Sciences and Engineering of the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences (LGSE-IHEG-CAGS). The laboratory analysis were carried out

following the analytical methods that were described by Huang et al. [20]. Major cations, including  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^+$ ,  $\text{Mg}^+$  were analyzed while using inductively coupled plasma-mass spectrometry (Agilent 7500ce ICP-MS, Tokyo, Japan).  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were measured by spectrophotometry (PerkinElmer Lambda 35, Waltham, MA, USA).  $\text{HCO}_3^-$  and TDS were determined by acid-base titration and gravimetric analysis, respectively. The percent charge balance errors of all samples were within  $\pm 5\%$ .

In order to get insight into the effects of evaporation on groundwater chemical composition, 29 groundwater samples were collected from shallow aquifer for analysis of deuterium and oxygen-18. Isotopic analysis of  $^2\text{H}$  and  $^{18}\text{O}$  were also performed at LGSE-IHEG-CAGS, following the methods described by Liu et al. [21]. The results were reported in  $\delta$  notation relative to the V-SMOW standard (Vienna Standard Mean Ocean Water) for oxygen and hydrogen, and the precision is within  $\pm 0.05\%$  and  $\pm 0.1\%$ , respectively.

### 3. Results and Discussion

#### 3.1. General Hydrochemical Characteristics

Table 1 lists the statistical analysis results of the physio-chemical indices of all samples. Groundwater pH is observed in the range of 7.20–8.40 in the shallow aquifer and ranges from 7.40 to 8.40 in the deep aquifer, suggesting that both shallow and deep groundwater in the study area is weakly alkaline water. TDS and EC of groundwater in the shallow aquifer are observed in the ranges of 266–1230 mg/L and 408–1869  $\mu\text{S}/\text{cm}$ , respectively, and those in the deep aquifer are 312–647 mg/L and 456–945  $\mu\text{S}/\text{cm}$ , respectively. The salinity of shallow groundwater is higher than that of deep groundwater.

Cations and anions show significant difference in shallow and deep groundwater. As shown in Table 1, the concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in shallow groundwater are observed in the ranges of 9.30–257 mg/L, 0.270–9.93 mg/L, 20.2–161 mg/L, 0.960–97.1 mg/L, respectively, and those in deep groundwater range within 6.40–139 mg/L, 0.240–5.14 mg/L, 22.2–82.6 mg/L, and 0.580–93.0 mg/L, respectively. For both shallow and deep groundwater,  $\text{Na}^+$  has the highest concentration value, followed by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and  $\text{K}^+$  has the lowest abundance. While the concentrations of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  in shallow groundwater are much higher than that in deep groundwater. Due to the high abundance of those cations in wastewater and reclaimed water [22], their use for irrigation results in elevation of the concentrations of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  in shallow groundwater [23]. The concentrations of  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$  in shallow groundwater range within 155–694 mg/L, 9.0–197 mg/L, and 12.3–167 mg/L, respectively. Those in deep groundwater are found in the range of 164–436 mg/L, 5.0–91.0 mg/L, and 8.80–86.2 mg/L, respectively. For both shallow and deep groundwater, the abundance of anions is in the following order:  $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ . Also, a higher abundance of anions is observed in shallow groundwater.

Nitrate is a very common groundwater pollutant in many regions in the world [24], and most of this contamination are from agriculture and sewage effluent containing high nitrate concentration [25,26]. In this study, the concentration of  $\text{NO}_3^-$  in shallow groundwater ranges from 0.15 mg/L to 19.3 mg/L with the mean value of 3.84 mg/L, and that in deep groundwater ranges within 0.20–3.83 mg/L with the average value of 0.91 mg/L. The upper geochemical limit for nitrate is 10 mg/L, any value exceeding the value is considered as pollution due to external factors [27]. Therefore, nitrate pollution was existed in the shallow aquifer, while no nitrate pollution has been found in the deep aquifer. While considering the maximum and mean value of nitrate in shallow groundwater, the nitrate pollution is not serious in the study area. Nitrite and ammonium can also indicate the groundwater pollution. The abundance of these two constituents in shallow groundwater is in the range of 0.00–1.21 mg/L and 0.02–4.11 mg/L, with the average value of 0.03 mg/L and 0.25 mg/L, respectively. While that in deep aquifer ranges within 0.00–0.09 mg/L and 0.02–0.50 mg/L with the mean value of 0.01 mg/L and 0.07 mg/L, respectively (Table 1). All above indicate that shallow groundwater has been polluted by nitrogen from agriculture and sewage effluent.

A Durov diagram (Durov 1948) was generated to examine the hydrochemical characteristics of groundwater in the study area (Figure 3). As shown in Figure 3, the majority of the deep groundwater samples have TDS less than 500 mg/L and HCO<sub>3</sub><sup>-</sup> is the dominant anion. While the shallow groundwater samples had a larger varied range of TDS content varying from 300 mg/L to 1300 mg/L, also dominated by HCO<sub>3</sub><sup>-</sup>. All the samples from both shallow and deep aquifers have similar concentration of cations. The larger varied range of TDS in shallow groundwater indicates that the quality of shallow groundwater is effected by evaporation and irrigated water infiltration. According to the Durov diagram, groundwater type in both shallow and deep aquifers in the area are mainly HCO<sub>3</sub>-Na·Mg·Ca, HCO<sub>3</sub>-Mg·Ca·Na, HCO<sub>3</sub>-Ca·Na, and HCO<sub>3</sub>-Na.

Table 1. Statistical analysis of groundwater samples.

	Index	Unit	Sample No.	Min	Max	Mean	SD	WHO Guideline (2011) [28]
Shallow GW	Ca	mg/L	44	20.20	161.00	85.19	35.28	75
	Mg	mg/L	44	0.96	97.10	48.88	23.42	50
	Na	mg/L	44	9.30	257.00	104.67	43.07	50
	K	mg/L	44	0.27	9.93	1.94	1.82	–
	HCO <sub>3</sub>	mg/L	44	155.00	694.00	470.34	131.39	500
	SO <sub>4</sub>	mg/L	44	9.00	197.00	80.91	47.65	250
	Cl	mg/L	44	12.30	167.00	65.08	41.73	250
	TDS	mg/L	44	266.00	1230.00	698.23	228.46	500
	EC	μS/cm	44	408.00	1869.00	1034.16	326.74	500
	pH	–	44	7.20	8.40	7.77	0.33	6.5–8.5
	NH <sub>4</sub> -N	mg/L	44	0.02	4.11	0.25	0.71	–
	NO <sub>2</sub> -N	mg/L	44	0.00	1.21	0.03	0.18	3
	NO <sub>3</sub> -N	mg/L	44	0.15	19.30	3.84	4.90	45
Deep GW	Ca	mg/L	43	22.20	82.60	42.08	11.99	75
	Mg	mg/L	43	0.58	93.00	20.73	14.05	50
	Na	mg/L	43	6.40	139.00	72.93	35.12	50
	K	mg/L	43	0.24	5.14	1.37	0.84	–
	HCO <sub>3</sub>	mg/L	43	164.00	436.00	283.19	67.60	500
	SO <sub>4</sub>	mg/L	43	5.00	91.00	45.59	19.17	250
	Cl	mg/L	43	8.80	86.20	24.27	14.41	250
	TDS	mg/L	43	312.00	647.00	383.88	67.12	500
	EC	μS/cm	43	456.00	945.00	622.37	97.10	500
	pH	–	43	7.40	8.40	8.07	0.30	6.5–8.5
	NH <sub>4</sub> -N	mg/L	43	0.02	0.50	0.07	0.12	–
	NO <sub>2</sub> -N	mg/L	43	0.00	0.09	0.01	0.01	3
	NO <sub>3</sub> -N	mg/L	43	0.20	3.83	0.91	0.88	45

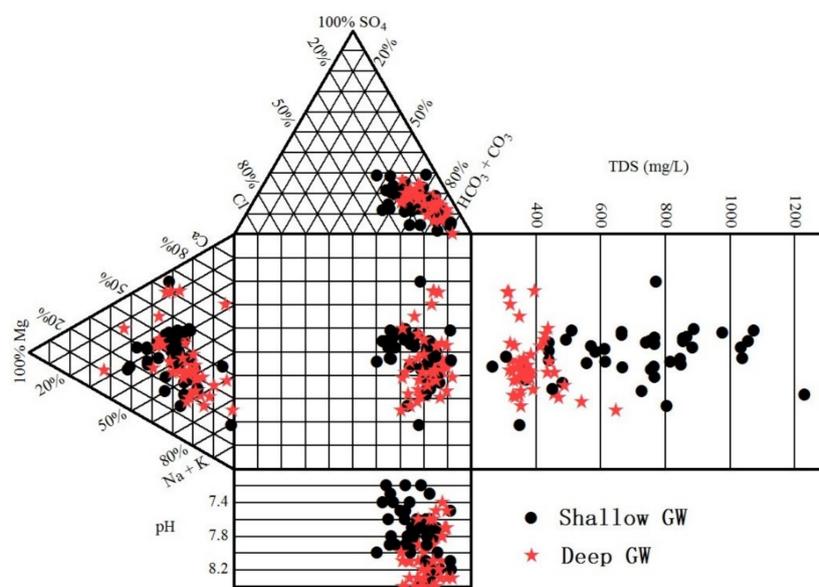
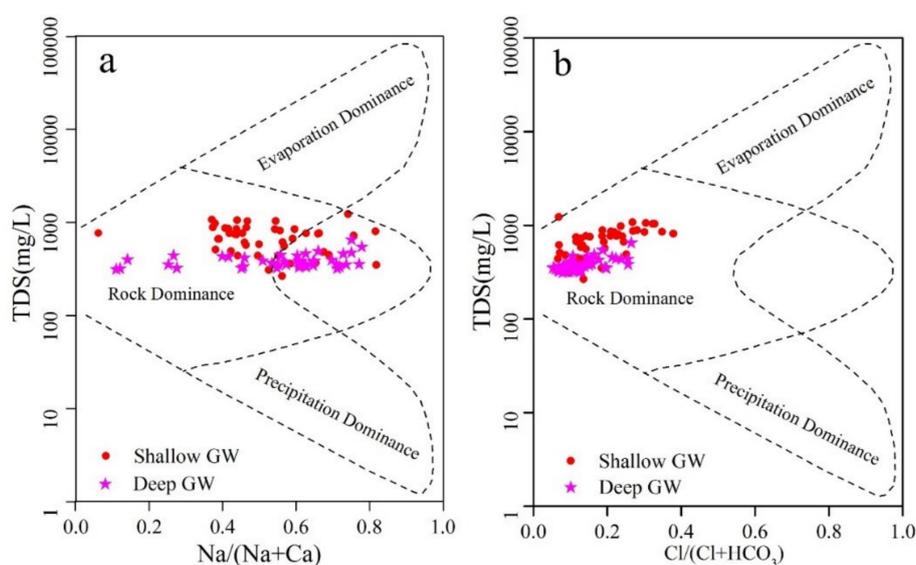


Figure 3. Durov diagram of groundwater samples.

### 3.2. Factors Controlling Groundwater Chemistry

Understanding the main factors controlling groundwater chemistry is very important for groundwater sustainable development. For studying the formation mechanism of groundwater, Gibbs diagrams [29], which divides the groundwater formation mechanism into rock, evaporation, and precipitation dominance, are used in the present study. As shown in Figure 4, all of the samples are plotted in the middle area of Gibbs diagrams, indicating that rock weathering is the main natural factor controlling groundwater chemistry in the study area. However, the trend of shallow groundwater samples, being plotted from rock dominance to evaporation dominance, indicating that evaporation is also responsible for shallow groundwater chemistry evolution in some degree [23]. It should be noted that Gibbs diagrams can analyze the main natural factors controlling groundwater evolution, but they are unable to identify the influence of human activities on groundwater chemistry.

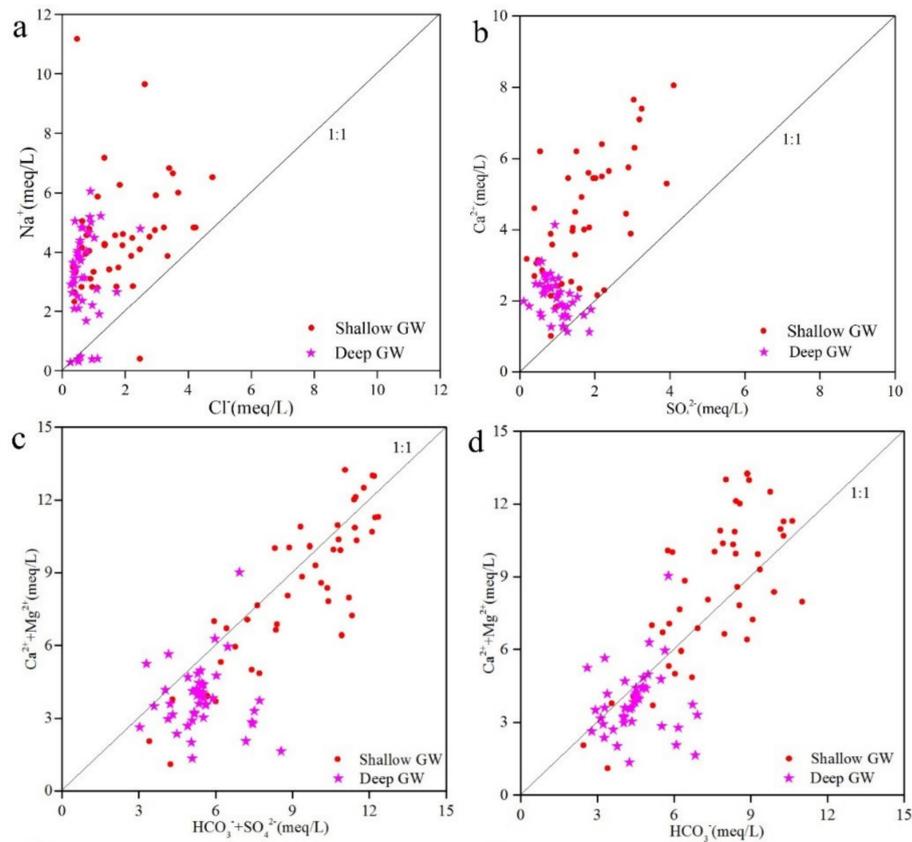


**Figure 4.** Gibbs diagrams showing the mechanism of groundwater evolution. (a) TDS vs.  $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ; (b) TDS vs.  $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ .

#### 3.2.1. Rock Weathering

To further refine the weathering processes of rocks, some bivariate plots of major ions were performed (Figure 5). Figure 5a shows that most groundwater samples are situated along the halite dissolution line, suggesting that halite dissolution may be a contributing factor to  $\text{Na}^+$  and  $\text{Cl}^-$  (1), as SI values of all the samples were less than 0 (Figure 6). However, most samples were observed deviating from the 1:1 line, indicates that the abundance of  $\text{Na}^+$  is also influenced by some other processes, such as ion exchange and silicate hydrolysis (2) [6,30].



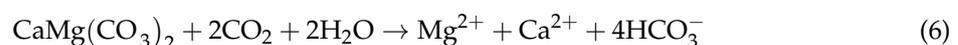


**Figure 5.** Bivariate plot of different ions showing the correlation of major ions to discriminate the chemical processes. (a)  $\text{Na}^+$  vs.  $\text{Cl}^-$ , (b)  $\text{Ca}^{2+}$  vs.  $\text{SO}_4^{2-}$ , (c)  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  vs.  $(\text{HCO}_3^- + \text{SO}_4^{2-})$ , (d)  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  vs.  $\text{HCO}_3^-$ .

As shown in Figure 5b,  $\text{Ca}^{2+}$  increases with  $\text{SO}_4^{2-}$  and the ratios of  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  are close to 1 in both shallow and deep groundwater, demonstrating that anhydrite and gypsum may be the sources of the two ions (3 and 4). All samples are under-saturated with the respect of anhydrite and gypsum (Figure 6), indicating that anhydrite and gypsum can continually dissolve in groundwater. While most samples fall above the 1:1 line (Figure 5b), suggesting that  $\text{Ca}^{2+}$  may also result from other chemical processes.



The plot of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  versus  $\text{HCO}_3^- + \text{SO}_4^{2-}$  can reveal the contribution of the dissolution of sulfates (such as anhydrite and gypsum) and carbonate minerals (such as calcite and dolomite) to groundwater chemistry (5) and (6). Figure 5c shows that majority of the samples falls along the 1:1 line, signifying that the dissolution of sulfates and carbonate minerals is the main source of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ , and  $\text{SO}_4^{2-}$  [31]. Figure 5d shows that most samples fall along the 1:1 line of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  versus  $\text{HCO}_3^-$  diagram, suggesting that the dissolution of carbonates is one of the potential contributions of  $\text{Ca}^{2+}$ . This is the reason that values of  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  of most samples are higher than 1 (Figure 5b). However, most samples are oversaturated with respect to calcite, aragonite, and dolomite, indicating that the dissolution of these three minerals is not the dominated contribution to  $\text{Ca}^{2+}$  in groundwater.



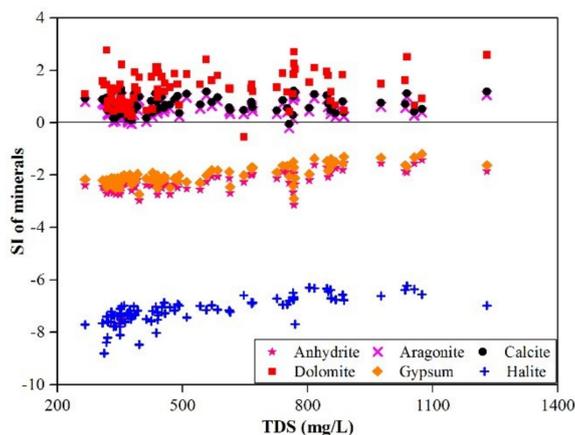


Figure 6. Relationships of saturation indices of selected minerals with total dissolved solids (TDS).

### 3.2.2. Ion Exchange

Cation exchange between  $\text{Na}^+$  and  $\text{Ca}^{2+}$  is an important natural process with significant influences on groundwater chemistry. Two chloro-alkaline indices (CAI-1 and CAI-2), as proposed by Schoeller [32], were introduced in the present study to examine the effects of cation exchange on groundwater chemistry. They are defined as following (all ions are expressed by meq/L):

$$\text{CAI-1} = \frac{\text{Cl}^- - (\text{Na}^+ + \text{K}^+)}{\text{Cl}^-} \tag{7}$$

$$\text{CAI-2} = \frac{\text{Cl}^- - (\text{Na}^+ + \text{K}^+)}{\text{HCO}_3^- + \text{SO}_4^{2-} + \text{CO}_3^{2-} + \text{NO}_3^-} \tag{8}$$

As shown in Figure 7a, about 94.25% of the samples had negative values of these two chloro-alkaline indices, indicating that exchange of  $\text{Ca}^{2+}$  with  $\text{Na}^+$  on aquifer materials (9) is the dominate cation exchange process in the study area. The bivariate diagram of  $(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})$  versus  $(\text{Na}^+ + \text{K}^+ - \text{Cl}^-)$  shows that most samples plot at lower right part of the diagram. It conforms a linear formula with the fitted slope of  $-0.923$ , confirming the existence of the exchange process expressed as R7. While the fitted slope is slightly lower than the theoretical value of  $-1$ , indicating that other processes also influence the concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  in groundwater [23].

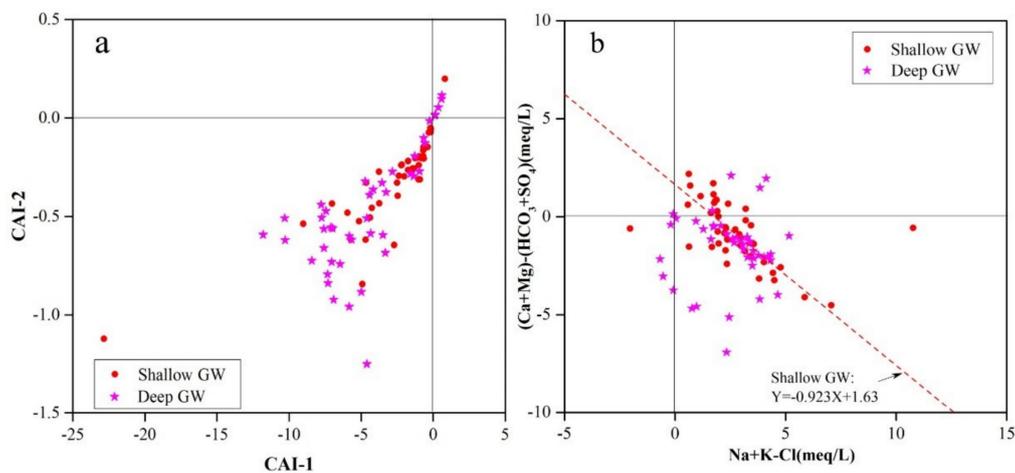
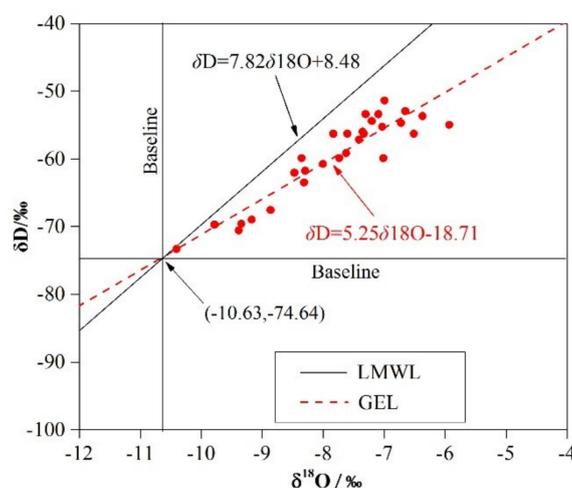


Figure 7. Plots of (a) CAI-1 against CAI-2 and (b)  $(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{SO}_4^{2-} + \text{HCO}_3^-)$  versus  $\text{Na}^+ + \text{K}^+ - \text{Cl}^-$ .

### 3.2.3. Evaporation

Evaporation is one of the important natural processes influencing groundwater chemistry in the study area. Deuterium and oxygen-18 isotopes are useful tools to get insight into the effect of evaporation on groundwater chemical composition. The relationship of  $\delta D$  and  $\delta^{18}O$  for shallow groundwater is plotted in Figure 8. As shown in Figure 8, all of the samples of shallow groundwater fall below the local meteoric water line (LMWL), as established by Song et al. [33], indicating the strong evaporation effect on shallow groundwater chemistry in this area. A groundwater evaporation line (GEL), being expressed as (10), was obtained from shallow groundwater samples.

$$\delta D = 5.25\delta^{18}O - 18.71 \quad (10)$$



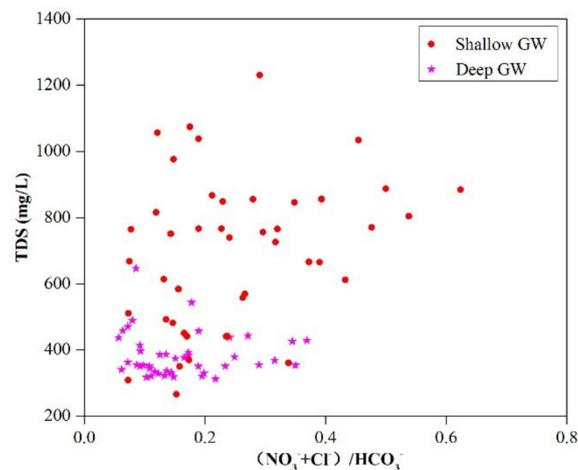
**Figure 8.** Plots of  $\delta^{18}O$  and  $\delta D$  of groundwater in the study area.

As shown in (10), the slope of GEL is smaller than that of LMWL, suggesting evaporation tends to enrich the heavy hydrogen and oxygen isotopes in shallow groundwater. Generally, the composition of hydrogen and oxygen stable isotopes in groundwater is rarely affected by water-rock interactions below 60 °C, and could remain relatively stable if there is no evaporation [23]. This means that the enrichment of heavy isotope can reflect the evaporation of groundwater in the area. Figure 8 shows that GEL intersects LMWL at  $(-10.63, -74.64)$ , and the values of this intersection are regarded as the baseline values of  $\delta D$  and  $\delta^{18}O$  for recharging rainfall in this area. As shown in Figure 8, all the samples are plotted at the right of baseline for  $\delta D$  and above the baseline for  $\delta^{18}O$ , confirming that shallow groundwater chemistry is also influenced by evaporation.

### 3.2.4. Human Activities

Human activities, such as wastewater effluents, irrigation, fertilizer application, and groundwater abstraction, have been found to have a great influence on groundwater quality [9,34,35]. Due to the complex and uncertainties of human activities, it is difficult to interpret the correlation between groundwater chemistry and human activities [1,23].  $NO_3^-$  is one of the common contaminations related to human activities in groundwater, being widely used to study the influences of human activities on groundwater chemistry [24,27]. As shown in Figure 9, TDS in shallow groundwater has positive correlation with  $(NO_3^- + Cl^-)/HCO_3^-$  and the Pearson correlation coefficient is 0.303 ( $p < 0.05$ ), indicating that shallow groundwater chemistry composition has been influenced by anthropogenic inputs [35]. While the correlation between TDS and  $(NO_3^- + Cl^-)/HCO_3^-$  in deep groundwater is not obvious, demonstrating that human activities have rare influences on deep groundwater quality. When considering the long history of wastewater and reclaimed water irrigation,

as well as fertilizer application, it is a common phenomenon that groundwater, especially shallow groundwater, have been polluted by anthropogenic pollutions [18,23,36].



**Figure 9.** Bivariate diagram of TDS versus  $(\text{NO}_3^- + \text{Cl}^-)/\text{HCO}_3^-$ .

### 3.3. Groundwater Suitability

#### 3.3.1. Drinking Purpose

Water quality index (WQI) is a simple and useful approach for determining the overall quality of groundwater and its suitability for drinking purposes, and it has been widely used over the world [37]. However, the traditional WQI approach uses empirical values as the weight of each chemical parameter without many valuable information of groundwater quality. Therefore, the results cannot reflect the truth of groundwater quality. In this study, an improved WQI approach with entropy weight (entropy weight water quality index, EWQI) was introduced to assess overall quality of groundwater. The procedures and details of EWQI have been described by Amiri et al. [38] as the Supplementary material. The drinking water standards (WHO 2011) [28] and overall groundwater quality classification criteria of EWQI are listed in Tables 1 and 2, respectively. The EWQI results of this study are shown in Figure 10.

As shown in Figure 10, most deep groundwater samples are placed in the “excellent” quality (rank 1), and the majority of the shallow groundwater samples are located in “good” and “medium” quality (rank 2 and 3). Among 43 deep groundwater samples, 31 are “excellent” quality (rank 1) water samples, and 12 are of “good” quality (rank 2), accounting for 72.09% and 27.91%, respectively. Among 44 shallow groundwater samples, 1 is of “excellent” quality (rank 1), 25 are of “good” quality (rank 2), and 18 are of “medium” quality (rank 3), accounting for 2.27%, 56.82%, and 40.91%, respectively. The calculation results of EWQI indicate that deep groundwater in the study area is excellent for drinking purposes, while shallow groundwater, with the water quality mainly ranging from good to medium, is not as excellent as the deep groundwater for drinking purpose. The difference of water quality between shallow and deep groundwater also confirms that human activities and evaporation are the responsible factors, resulting in the relative poor quality of shallow groundwater.

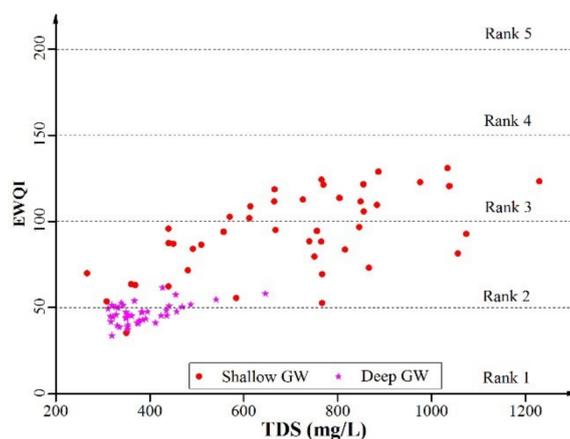


Figure 10. Bivariate diagram of entropy weighted water quality index (EWQI) versus TDS.

Table 2. Classification criteria of groundwater quality base on EWQI.

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

### 3.3.2. Irrigation Purpose

Groundwater suitability for irrigation mainly depends on the concentration of total salinity and sodium related to other ions [39]. Therefore, salinity hazard and sodium hazard are the core issues concerned in irrigation water quality assessment. In this study, the suitability of groundwater for irrigation is evaluated by electrical conductivity (EC), adsorption ratio (SAR), solute sodium percentage (%Na), and Permeability index (PI). Table 3 lists the criteria of irrigation water quality classifications that are based on EC, SAR, and %Na [40].

EC, a measure of the total salinity, is usually used to classify irrigation water quality. According to the criteria based on EC (Table 3), 86.36% and 13.64% of deep groundwater samples had EC values ranging from 250  $\mu\text{S}/\text{cm}$  to 750  $\mu\text{S}/\text{cm}$  and between 750  $\mu\text{S}/\text{cm}$  and 2250  $\mu\text{S}/\text{cm}$ , respectively (Figure 11), indicating good and acceptable quality for irrigation; and, 23.26% and 76.74% of shallow groundwater samples are with EC values in the range of 250–750  $\mu\text{S}/\text{cm}$  and 750–2250  $\mu\text{S}/\text{cm}$  (Figure 11), respectively, demonstrating good and acceptable quality for irrigation. The quality of deep groundwater is better than shallow groundwater for irrigation with respect to EC values.

Table 3. Criteria of irrigation water quality classifications based on EC, SAR, %Na and RSC.

EC	SAR	Irrigation Water Quality	%Na	Irrigation Water Quality
<250	<10	Excellent	<30	Suitable
250–750	10–18	Good	30–60	Marginally suitable
750–2250	18–26	Acceptable	>60	Unsuitable
>2250	>26	Unacceptable		

SAR is a measure of soil capacity to adsorb sodium from agricultural irrigation water and thus a significant parameter to determine possibility of sodium/alkali hazard to crops. SAR is obtained using (11). The concentrations of all ions in (11) are expressed in meq/L. According to the criteria that

are based on SAR in Table 3, all the samples of shallow and deep groundwater in the study area had excellent quality for irrigation.

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \tag{11}$$

United States Salinity Laboratory (USSL) diagram [41] was applied to evaluate the suitability of water for agricultural irrigation purpose in this study. As shown in Figure 11, 23.26%, 72.09%, and 4.65% of shallow groundwater samples are plotted in C2S1 (medium salinity with low sodium hazard), C3S1 (high salinity with low sodium hazard), and C3S2 (high salinity with medium sodium hazard), respectively; and, 86.36% and 13.64% of deep groundwater fall in the C2S1 and C3S1, respectively. All of the above indicates that both shallow and deep groundwater are with good to acceptable quality for agricultural purpose, but deep groundwater is more suitable for irrigation than shallow groundwater.

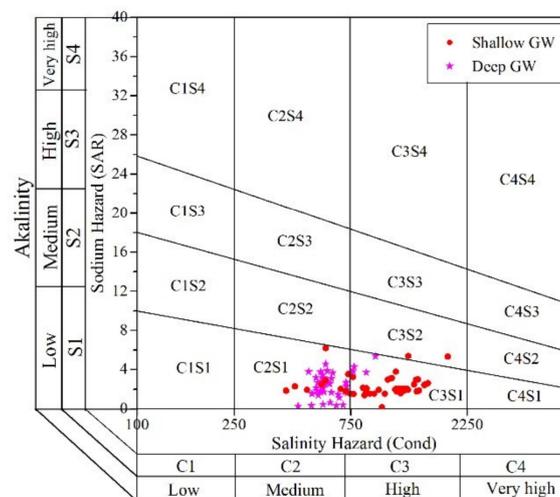


Figure 11. USSL diagram for groundwater in shallow and deep aquifers.

%Na is another important parameter to indicate the suitability of water for irrigation. It is calculated by (12). All the cations in Equation (12) are expressed in meq/L. According to the Wilcox diagram (Figure 12), 20.93%, 72.09%, and 6.98% of shallow groundwater samples belong to excellent to good, good to permissible, permissible to suitable categories for irrigation, respectively; and, most of the deep groundwater samples (88.64%) belong to the excellent to good category, while 4.55% and 6.82% belong to good to permissible and permissible to suitable categories, respectively.

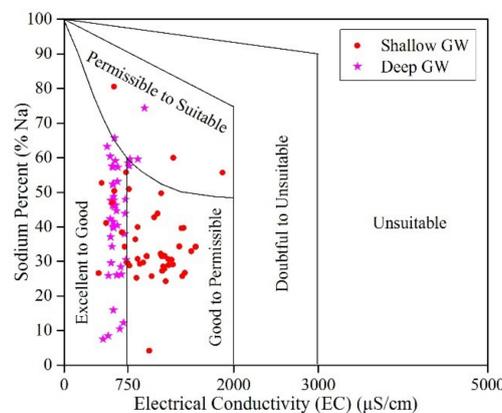


Figure 12. Wilcox diagram (%Na vs. EC) for assessing Irrigation water quality.

$$\%Na = \frac{Na^+}{Ca^{2+} + Mg^{2+} + Na^+ + K^+} \quad (12)$$

Permeability is an important physical property of soil that may be influenced by long-term use of irrigation water [5]. Permeability index (PI), which represented by (13), is widely used to determine the influence of long-term irrigation on soil hydraulic property [42]. According to PI values, irrigation water is divided into three classes: Class-I is of excellent quality, Class-II is acceptable for irrigation, and Class-III is unsuitable water for irrigation. As shown in Figure 13, 86.05% of shallow groundwater samples are classified into Class-I, 11.63% into Class-II, and 2.33% into Class-III; 18.18%, 75.00%, and 6.82% of deep groundwater samples belong to Class-I, II, and III, respectively. The classified results indicate that most of the shallow and deep groundwater samples are suitable for long-term irrigation without influence on soil property, except one shallow and three deep groundwater samples.

$$PI = \frac{Na^+ + \sqrt{HCO_3^-}}{Ca^{2+} + Mg^{2+} + Na^+} \times 100\% \quad (13)$$

Overall, both shallow and deep groundwater are suitable for irrigation purpose and they may not induce salinity and sodium hazard. However, there are one shallow and three deep groundwater samples with high PI values, the long-term use of which may affect the soil property and influence the yields of crop. Therefore, the long-term use of these four groundwater samples for irrigation should be avoided.

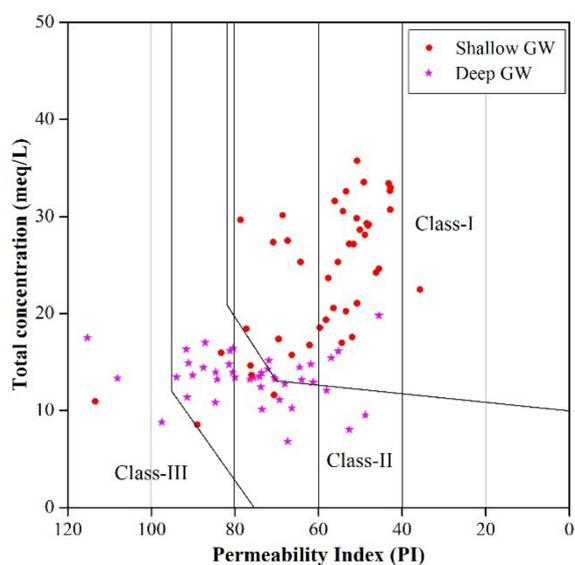


Figure 13. Classification of irrigation water based on permeability index.

#### 4. Conclusions

The shortage of water sources led to long-term use of wastewater and reclaimed water for irrigation in the semi-arid regions, and it may threaten the quality of groundwater as well. In the present study, factors influencing groundwater chemistry and its quality in Beijing were discussed in detail. Groundwater quality assessments were also introduced to evaluate the suitability for drinking and irrigation purpose. The achieved conclusions were following:

Groundwater in both shallow and deep aquifers in the study area is weakly alkaline freshwater. The abundance is in the order  $Na^+ > Ca^{2+} > Mg^{2+} > K^+$  for cations, and  $HCO_3^- > SO_4^{2-} > Cl^-$  for anions, resulting that the water types of both shallow and deep groundwater were dominated by  $HCO_3-Na \cdot Mg \cdot Ca$ ,  $HCO_3-Mg \cdot Ca \cdot Na$ ,  $HCO_3-Ca \cdot Na$  and  $HCO_3-Na$ .

Water-rock interactions, including rock weathering and ion exchange are the dominant factors controlling groundwater chemistry in both shallow and deep aquifers. The dissolutions of halite, gypsum, anhydrite, silicates and ion exchange are the main reactions forming composition for both shallow and deep groundwater. While shallow groundwater chemistry is also influenced by evaporation and anthropogenic inputs.

Quality assessment reveals that groundwater in both shallow and deep aquifers, in general, is suitable for drinking and irrigation purpose. According to the results of EWQI, the quality of shallow groundwater for drinking is mainly good to medium, and that of deep groundwater is better, showing dominantly excellent. The assessments based on SAR, %Na, USSL classification, and Wilcox diagram show that both shallow and deep groundwater are of excellent to good categories for irrigation use without severe hazards, but the PI values indicate that one shallow groundwater and three deep groundwater have risks of soil quality deterioration. Groundwater in these locations should be avoided for agricultural irrigation. Overall, it is recommended that deep groundwater is preferentially used for drinking and domestic purpose, and shallow groundwater for agricultural irrigation.

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