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Hydrogeochemical Assessment of Groundwater in the Southeast of Benghazi City, Libya

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A B S T R A C T

Libya is situated in an arid region of northern Africa, and faces significant water scarcity, making water one of the most essential resources in the whole country. Therefore, to achieve water security in Libya, surface and groundwater resources must be assessed, protected, and kept uncontaminated. This paper evaluates the hydrochemistry, water quality, and the possibility of use for various purposes of the groundwater in the area southeastern of Benghazi city. Some hydrogeochemical relations such as Piper, Gibbs, Salinity, and Wilcox diagrams were employed to determinate the origin, type, and property of the groundwater, also; to know the different uses of this groundwater and the relationships between the chemical variables. Phreeqc software also has been used to know the saturation index (SI) of the water with minerals of the aquifer's rocks, as it indicated that the groundwater is slightly saturated with carbonate minerals and under-saturated with evaporate minerals. In general, the studied groundwater is salty to highly salty, holding high concentrations of the total dissolved solids (TDS), and is dominated by sodium and chloride "primary salinity" water type, in response to rock weathering and water-rock interaction as they are the most natural processes controlling groundwater chemistry. However, the water is highly salty and unsuitable for drinking, but it can be potentially utilized for the irrigation of some select crops to contribute to sustainable water resource utilization in the region.

التقييم الهيدروجيوكيميائي للمياه الجوفية في جنوب شرق مدينة بنغازي، ليبيا

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الكلمات المفتاحية:
المعادن
المياه العذبة
الهيدروكيمياء
جودة المياه
خزانات المياه الجوفية
مؤشر التشبع بالمعادن

الملخص

تقع ليبيا في منطقة قاحلة في شمال قارة أفريقيا، وتواجه ندرة كبيرة في المياه، مما يجعل المياه الجوفية واحدة من أهم الموارد المائية في البلاد. ولتحقيق الأمن المائي في ليبيا، يجب تقييم موارد المياه السطحية والجوفية وحمايتها وإبقائها صالحة للاستخدام وغير ملوثة. تقوم هذه الورقة بتقييم الوضع الهيدروكيميائي في منطقة الدراسة الواقعة جنوب شرق مدينة بنغازي، وتحديد نوعية المياه ومدى إمكانية استخدام هذه المياه الجوفية للأغراض المختلفة، حيث تم في هذه الدراسة استخدام بعض المخططات الهيدروجيوكيميائية مثل مخططات بايبر، وجيبس، والملوحة، وويلكوكس لمعرفة أصل ونوع وخصائص المياه الجوفية، وتحديد الاستخدامات المتنوعة لهذه المياه وكذلك معرفة العلاقات بين المتغيرات الكيميائية المختلفة. تم أيضاً استخدام برنامج Phreeqc لمعرفة مؤشر تشبع المياه بمعادن صخور الخزان الجوفي، حيث تبين أن المياه مشبعة قليلاً بمعادن صخور الكربونات وناقصة التشبع بمعادن صخور المتبخرات، وبشكل عام تعتبر المياه الجوفية في منطقة الدراسة مالحة إلى شديدة الملوحة وتحتوي على تركيزات عالية من إجمالي المواد الصلبة الذائبة، ويغلب عليها تركيزات عناصر الصوديوم والكلوريد ونوع ملوحة المياه هو "الملوحة الأولية"، وذلك استجابة لعمليات التجوية الصخرية في تلك المنطقة وكذلك التفاعل ما بين المياه الجوفية وصخور الخزان الجوفي، حيث كانت هذه العمليات هي أكثر العمليات الطبيعية المتحكمة في كيمياء المياه الجوفية، ومع ذلك تعتبر المياه شديدة الملوحة وغير صالحة للشرب، ولكن يمكن استخدامها لري بعض المحاصيل الزراعية المعينة للمساهمة في الاستخدام المستدام للموارد المائية في المنطقة.

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1. Introduction

Water is a crucial and vital natural resource for irrigation and drinking, it forms the core of the ecological system [1]. The demand for groundwater is growing with the increase in population growth, consumption, and pollution of surface water bodies by agriculture and industrialization. Protecting these resources is one of the greatest difficulties facing humanity [2]. The chemical composition of the groundwater plays a significant role in the water quality evaluation and the range of permissible limits for drinking and irrigation [3]. Libya is one of those countries that suffers from a severe shortage of surface and groundwater resources due to its location in the arid and semi-arid regions in the northern part of Africa, which suffers from little precipitation and high evaporation rates. The groundwater wells in Libya are the main resource for drinking and irrigation purposes, which may contain contaminants, and then become harmful to humans. Therefore, looking for groundwater sources and protecting it is a very important demand [4]. To achieve water security, this work aims to assess and evaluate the groundwater quality of the eight groundwater wells in the study area and investigate their suitability for human and agricultural uses. The study area, which is considered an agricultural area, is located in the southeast of Benghazi city, northeast Libya (Fig. 1). This study is based on the measuring of different chemical parameters of the groundwater from the selected wells such as concentrations of major ions, heavy metals, hydrogen potential (pH), total dissolved solids (TDS) and electrical conductivity (EC).

2. Geological settings

The research area is situated in the structural element of the Soluq Depression in the southwestern part of Al Jabal al Akhdar [5]. The area is composed of carbonate rocks, mainly limestone with minor dolostone, interbedded with clay and gypsum. The stratigraphy of the study area based on Klen [6] in ascending order are: i) Benghazi Formation: It is exposed throughout several places in the coastal plain to the south of Benghazi city, and consists mainly of limestone with small patches of green fossiliferous clay. ii) Wadi al Qattarah Formation: It is unconformably overlies Benghazi Formation and consists of limestone, mostly oolitic grainstone in texture. iii) Quaternary deposits: They consist of different types such as littoral marine, lagoonal, Sebkha, and alluvial deposits [5]. An important phenomenon is the spreading of the karstification features in the region and their contribution to groundwater movement in limestone, this is particularly apparent in the limestones of the Benghazi Formation of the Ar-Rajmah Group [7], There are many Doline lakes with brackish water in the coastal plain of the Benghazi region which are part of the karstified features [6]. Abdelmalik et al., [7] are supporting the groundwater movement through a vast cavernous system onto the coast. Hence, the salinity of groundwater becomes more deteriorated throughout the Benghazi plain as getting closer to the sea coast .

3. Materials and Methods

Eight groundwater samples (S1, S2, S3, S4, S5, S6, S7, and S8) were collected in polypropylene bottles while the groundwater wells were pumping to ensure representative sampling. Electrical conductivity (EC), potential of Hydrogen (pH), and Temperature (T) were determined in situ using HANNA Instrument. The chemical analyses were completed in the laboratory of the Water General Authority (WGA) in Benghazi (Appendix 1). The variables of the analysed samples were calculated and compared to the permissible of the drinking water quality with world standards. In this study, the Piper, Gibbs, Salinity, and Wilcox diagrams are used to determinate the different relations between the chemical variables. The origin and water type were also determined to know the water properties quality and their suitability for drinking, household uses, and irrigation purposes. Furthermore, the saturation index (SI) was calculated using the PHREEQC interactive code by applying the equation :

$$\mathbf{SI = \log [ion\ activity\ product] / KT}\ [8]$$

where KT = equilibrium constant at a given temperature T (Co).

The sodium percentage Na% was calculated as :

$$\mathbf{Na^{+}\% = 100\ (Na^{+} + K^{+}) / (Ca^{+2} + Mg^{+2} + Na^{+} + K^{+})}$$

where the Na% is compared to the Electrical Conductivity (EC) when used in the Wilcox diagram of water quality classification to assess how well water is appropriate for irrigation requirements.

4. Results and discussion

4.1. The groundwater chemistry composition

Groundwater quality is affected by the elemental composition of the aquifer's rocks and the water-rock interactions, ion exchange, and silicate/carbonate weathering [9]. In addition, the geochemical processes are controlled by the chemical makeup of groundwater when it flows and reacts with the geologic materials of the aquifers [10]. The chemical analyses of the studied groundwater samples showed that all chemical parameters fell within the acceptable limits of the and the Libyan National Centre for Standardization and Metrology (LNCSM) [11] and World Health Organization (WHO) [12] except the total dissolved solid, magnesium, sodium, and chloride (Table 1). The Hydrogen potential (pH) and electrical conductivity (EC) levels of groundwater range from 7.1 to 8.4 and 1675 to 2920 μS/cm, respectively. The total dissolved solids (TDS) varied between 1088 to 1825 mg/l, where all the groundwater samples fell in the range of brackish water type (1000 - 10000 mg/l) [13] (Table 2). Sodium and chloride are the dominant ions "cations and anions", respectively, this results from the seawater intrusion, which increases the concentration of these two elements (Fig. 2) .

4.2. Saturation Indices of the Groundwater

To recognize the changes in water chemistry, and the dissolved minerals in the water and to address the variation of these minerals along the groundwater flow stream, a scenario using the PHREEQC interactive code was achieved by applying the equation [8]. The saturation indices (SI) of the studied groundwater's dissolved minerals have been calculated by using this simulation. The saturation index (SI) is specified as the logarithm of the ratio of ionic activity products (IAP) to the solubility product (Ksp) at a specified temperature. The ability of groundwater to dissolve or precipitate minerals could be studied using the saturation indices via the PHREEQC interactive code [14]. In general, the groundwater-rock equilibrium is typically attained when SI = 0, if SI is greater than 0, the water is supersaturated, and precipitation of minerals is required to reach equilibrium, while if SI is less than 0, the water is undersaturated, and mineral dissolution is necessary to achieve equilibrium [15]. All the studied groundwater samples are saturated to slightly saturated concerning dolomite, calcite, and aragonite, while the groundwater is undersaturated with respect to gypsum and anhydrite, and undersaturated for halite and sylvite (Fig. 3). This situation results from the groundwater flow and the interactions between groundwater and the minerals of the surrounding aquifer rocks, due to the carbonate and evaporation rocks are the main types of the rocks of the aquifer .

4.3. Piper diagram

The Piper diagram was designed in (1944) and is an indicator used to estimate the chemical affinity of water samples and potential effective processes in aquifers based on the equivalent ratios of alkali metals and alkaline earths versus strong and weak acidic anions [16]. Piper diagram was applied to the chemical analyses of the groundwater samples of the study area to know its water type, origin, and the processes that affected the groundwater composition and the factors controlling the hydrogeochemical conditions in the aquifer, and the diagram has shown that six of the studied groundwater samples are located in the Na^{+}–Cl^{-} type and two samples in the portion of mixed type, indicating that there is not cation-anion pair exceeding 50 %. The alkaline earths (Ca^{+2}+Mg^{+2}) exceed alkalis (Na^{+}+K^{+}) and strong acids exceed weak acids (Fig. 4).

4.4. Gibbs diagram

Gibbs diagrams are frequently utilized to determine the origins of the dissolved chemical elements in groundwater and comprehend the parameters governing groundwater chemistry [17]. Gibbs diagrams include two diagrams in each one there are three distinct zones, evaporation crystallization, rock weathering, and precipitation. The first diagram shows the ratio of Na^{+}, Cl^{-}, and $HCO3^{-}$ on the x-axis and TDS on the y-axis with a logarithmic scale, the second diagram shows the relative concentrations of Cl^{-}, $HCO3^{-}$ on the x-axis and TDS on the y-axis with a logarithmic scale. The studied groundwater samples are dominated by sodium, chloride, and bicarbonates, the samples fall in the rock weathering zone of the Gibbs diagram (Fig. 5), which indicates the groundwater-rock interaction, which is a natural process control of the chemistry of groundwater.

4.5. The groundwater appropriateness for Drinking

The groundwater assessment for drinking suitability and domestic purposes is based on the total dissolved solids (TDS) and the concentrations of major ions. According to the water type classification of [13], all the studied groundwater samples are situated in hard to very hard categories of hardness and it is a brackish water type; thus, this water is not suitable for drinking and human consumption. Based on the standard limits for drinking given by Libyan National Centre for Standardization and Metrology (LNCSM) [11] and World Health Organization (WHO) [12], the TDS values of studied groundwater samples are unsuitable for drinking as those limits have been exceeded .

4.6. The groundwater appropriateness for irrigation purposes

The suitability of water for farming usage could be assessed by using some calculation ratios, such as US Salinity and Wilcox's diagram which shows the relationship between sodium concentrations and the salinity value in the water.

4.6.1. Salinity index

The US Salinity Laboratory Staff [18] designed a diagram (us salinity diagram) that classified the groundwater based on salinity (represented in terms of EC) on the X-axis and sodium hazards (represented in terms of SAR) on the Y-axis, then the diagram was modified by [19] where they extended the water salinity up to 30000 µS/cm. Based on the US salinity diagram, the studied groundwater samples have extremely high salinity and fall in the C4-S2 class which is considered by very high salinity and intermediate sodium hazard, and in the C4-S3 class (Appendix 2) [20], which is characterized by extremely high salinity and high sodium hazard, which means the groundwater can be used for some types of soil with little risk of sodium absorption (Fig. 6). This increase in salinity and sodium hazard is due to the seawater intrusion resulting from the high groundwater extraction in the study area, also; to the chemical composition of the rocks of the aquifers.

4.6.2. Wilcox diagram

Wilcox diagram [21] shows the relationship between electrical conductivity (EC) on the X-axis and sodium percent (Na^{+}%) on the Y-axis, the diagram easily visualizes the appropriate of groundwater for irrigation intention. Based on the Wilcox diagram, all the analysed groundwater samples are situated in the allowable to doubtful and doubtful to unsuitable classes, indicating their suitability for irrigation for some special crops (Fig. 7).

5. Conclusions

This study has investigated the prevailing hydrogeochemical processes and the quality evaluation of the groundwater of area southeastern of Benghazi city. In general, seawater intrusion, evaporation, and the connection between water and rocks are the main factors controlling groundwater quality. The chemical analysis of the studied groundwater samples shows that the water is a brackish water type, the sodium, and chloride (Na^{+}–Cl^{-}) represent the main water type and shows that all chemical parameters of the groundwater are within the acceptable limits of WHO except the TDS, Na^{+}, Mg^{+2}, and Cl^{-}. The groundwater of the study area is classified as hard to very hard and contains high TDS which indicates its unsuitability for drinking. In terms of the appropriateness of groundwater for farming and agricultural purposes, the groundwater of the study area is situated in the allowable to doubtful and doubtful to unsuitable classes for irrigation for some special crops. The groundwater is saturated to slightly saturated concerning dolomite, calcite, and aragonite minerals, while it is undersaturated regarding gypsum and anhydrite minerals, and it is undersaturated regarding halite and sylvite minerals, due to interactions between groundwater and surrounding rock materials of the aquifer.

6. Recommendations

- The heavy extraction of the groundwater should be reduced slightly to avoid more water quality deterioration.
- The desalination process of the groundwater is of necessary before using for drinking.
- The chemical analysis is very important to investigate the seawater intrusion into the aquifers of the coastal stripe of the Benghazi area and the whole Libyan coast.

7. Appendixes

Appendix 1. Results of the major element analysis of studied groundwater samples (Element concentrations, TH and TDS are in mg/l, temperature is in degree Celsius and EC is in µS/cm.

Sample No.	Depth (m)	T H	Temp.	E C	pH	TDS	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}
S1	100	1125	24	2920	8.37	1825	91	92	433	18	822	224	196
S2	145	1016	24	2241	8.15	1355	86	71	413	16	730	213	184
S3	204	463	24	1770	7.83	1153	80	64	259	12	585	70	165
S4	233	423	24	1675	7.62	1088	104	60	231	11	604	66	158
S5	251	350	24	2340	7.19	1356	80	36	368	25	505	197	290
S6	273	364	24	2025	7.24	1296	94	54	322	20	587	176	254
S7	250	350	24	2340	7.19	1356	80	36	368	25	505	197	290
S8	266	372	24	2035	7.12	1322	103	43	386	27	566	202	326

Appendix 2. USSL diagram Classes for irrigation purposes [20].

	Salinity Hazard
C1	Used for irrigation of most crops on most soils with little development of soil salinity.
C2	Used if a moderate infiltration can occur. Plants with moderate salt tolerance can be grown without special salinity control.
C3	Cannot be used on soil with restricted drainage and poor infiltration, special salinity control may be required and plants with good tolerance should be selected.
C4	Not suitable for irrigation under ordinary conditions but may be used in special cases (soil must be permeable, drainage must be good and irrigated water must be applied in excess to provide considerable infiltration). Only very salt tolerance plant should be selected.
	Sodium Hazard
S1	Used for irrigation under ordinary circumstances on all soil with little development of harmful levels of sodium content, whereas sensitive sodium crops as avocados and stone fruit trees may accumulate harmful concentrations of sodium.
S2	It shows a remarkable sodium hazard in fine textured soils which have cation exchange capacity and low infiltration unless gypsum is applied in the soil. This water may be used in coarse textured soil or organic soils with good permeability.
S3	It produces harmful sodium content in most soils. Its use requires good drainage, high infiltration, high organic conditions, and soil amendments. Chemical amendments may be not suitable for very high salinity waters.
S4	It is unsatisfactory for irrigation uses except at low and perhaps medium salinity. Gypsum as soil amendment may facilitate the use of this class in irrigation.

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Figures and Tables

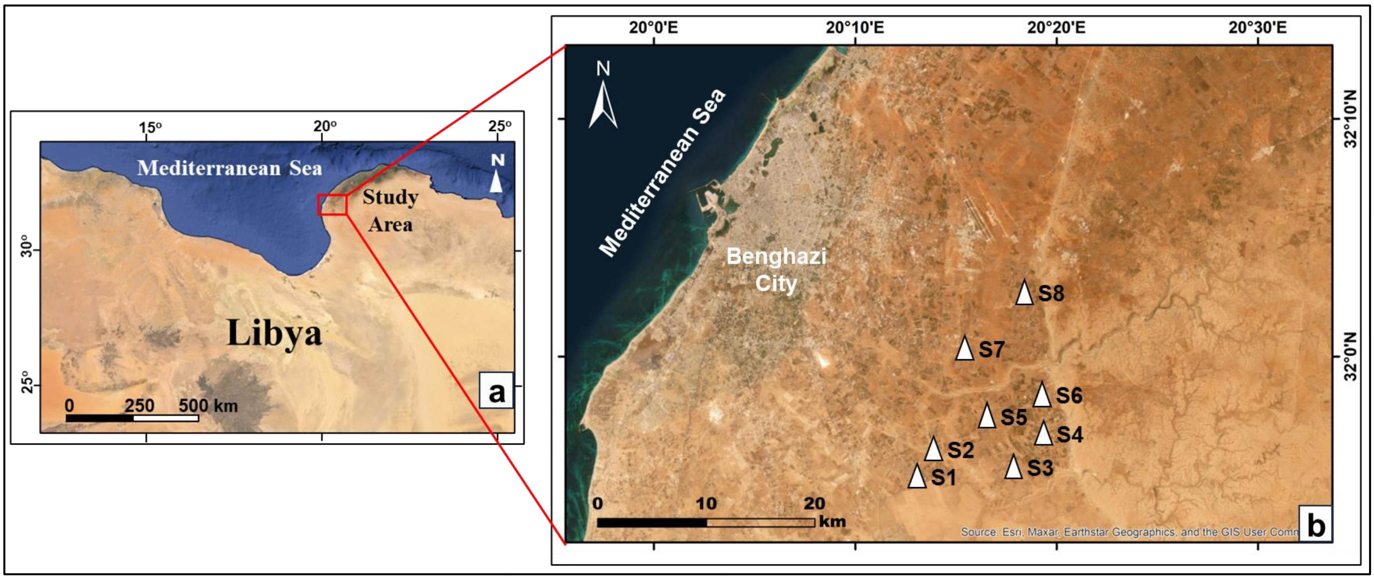

Fig. 1: Satellite images: a) Index image of the study area, b) location of the studied groundwater wells SE of Benghazi city.

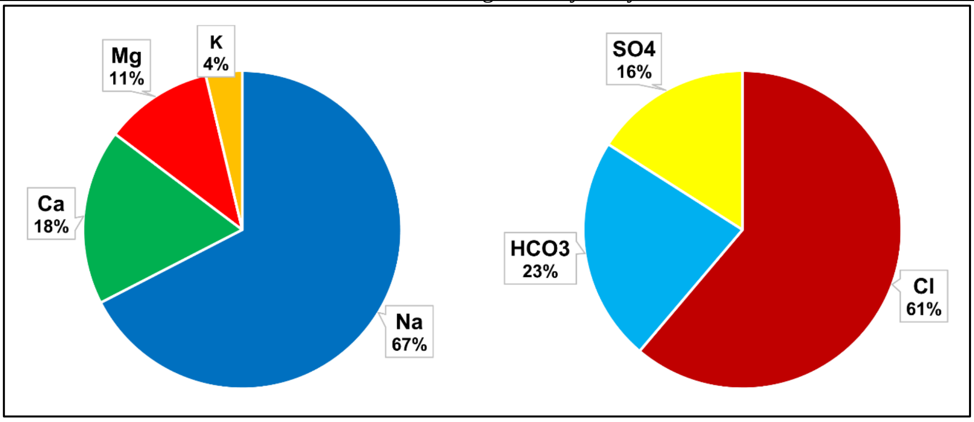

Fig. 2: Pie diagrams of the chemical element's values of major ions in the studied groundwater samples.

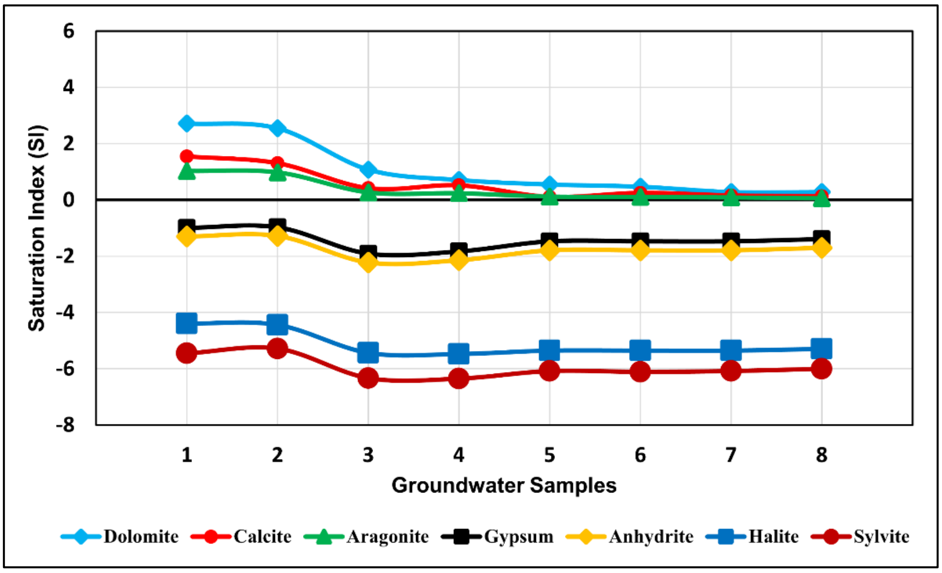

Fig. 3: Minerals saturation indices values of the studied groundwater samples.

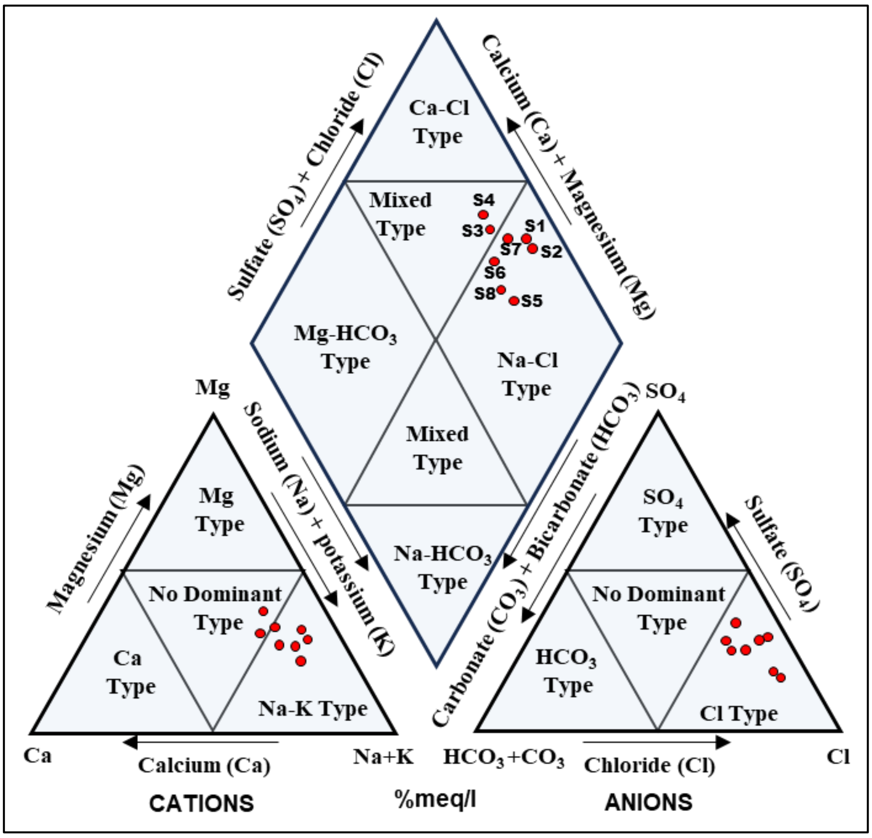

Fig. 4: Piper diagram showing the hydrochemical facies of the studied groundwater samples.

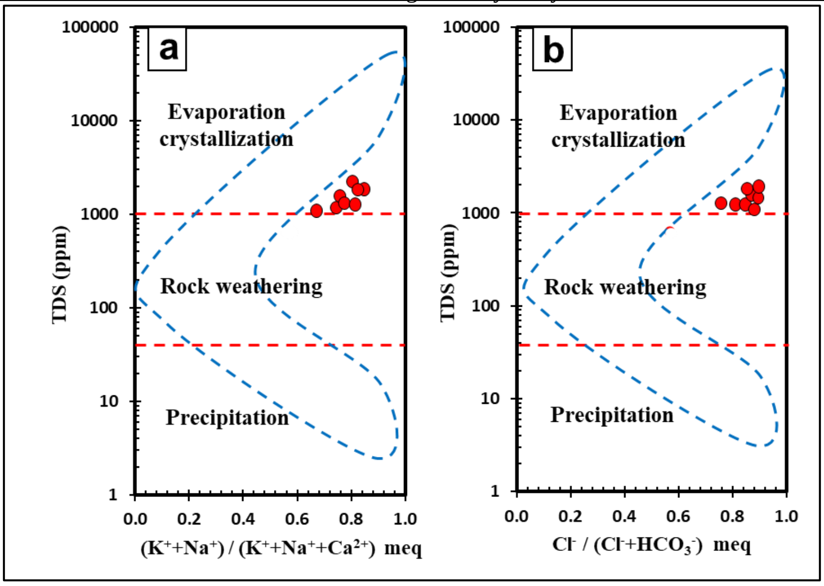

Fig. 5: Gibbs diagram showing the hydrogeochemical processes affecting water chemistry using a) cations and b) anions

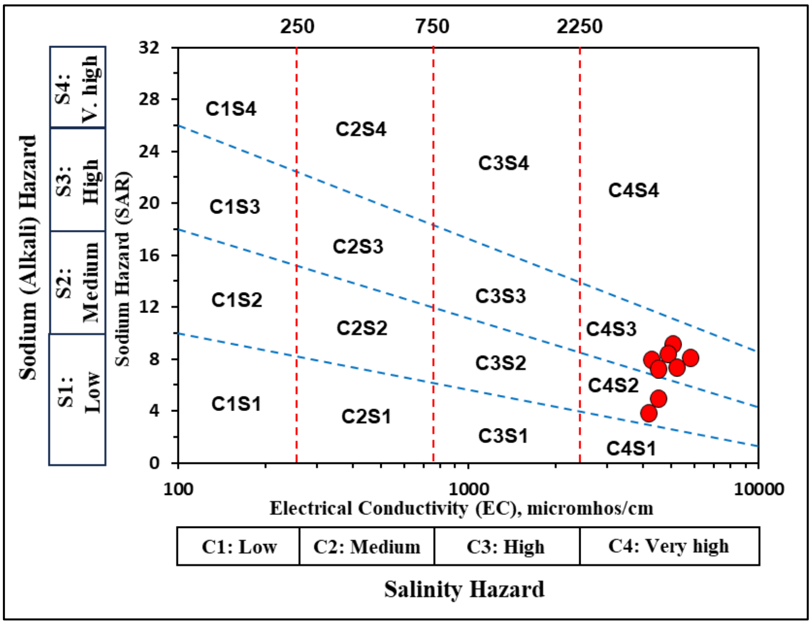

Fig. 6: US Salinity diagram showing the classification of the irrigation purposes for the studied groundwater samples.

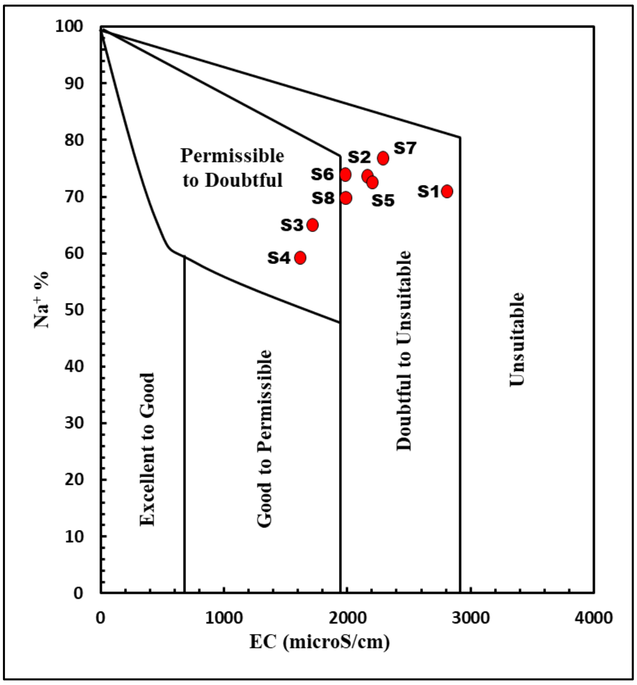

Fig. 7: Wilcox diagram showing the classes of irrigation for the studied groundwater samples.

Table 1: Descriptive statistics of the analysed groundwater samples. Element concentrations and TDS are in mg/l; EC is in µS/cm; and temperature in C°. Guidelines of drinking water quality of LNCSM (2020) and WHO (2018) standards.

Parameters	Min	Max	Average	LNCSM	WHO
Temp.	24	24	24	-	-
EC	1675	2920	2194	-	-
pH	7.1	8.4	7.6	6.5 - 8.5	6.5 - 8.5
TDS	1088	1825	1366	500	500
Ca^{2+}	80	104	90	150	200
Mg^{2+}	36	92	58	50	50
Na^{+}	231	433	344	100	200
K^{+}	11	27	19	50	50
Cl^{-}	505	822	623	150	250
$SO4^{2-}$	66	224	164	200	600
HCO_3^{-}	158	326	235	400	600

Table 2: Classification of water types on the basis of TDS values [13].

Water Class	TDS (mg/l)
Fresh water	< 1000
Brackish water	1000 – 10000
Saline water	10000 - 100000
Brine water	>100000