

GIS and Index-Based Methods for Assessing the Human Health Risk and Characterizing the Groundwater Quality of a Coastal Aquifer

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ABSTRACT

The massive dune aquifer of Bouteldja is one of the most exploited aquifers in Algeria; as a result, its piezometric level has declined. Such pressure on the dune aquifer, in addition to its moderate-to-severe vulnerability to pollution, may lead to deterioration of groundwater quality. This study is intended to assess the quality of aquifer groundwater for drinking, irrigation and industrial purposes, and also to evaluate health risks. To this end, we analyzed data of 16 physicochemical parameters collected from 25 groundwater samples. Using the Durov diagram, principal component analysis (PCA), and Pearson's correlation matrix, we found that most major ions show similar origins related to ion exchange and the proximity of the sea. Our results showed that, overall, the groundwater intended for drinking purposes was of good or excellent quality over most the aquifer, where the majority of wells are located. However, the groundwater is mostly unsuitable for irrigation purposes according to the Kelly index (KI), percentage of sodium (Na %), magnesium hazard (MH), and irrigation water quality index (IWQI). Further, calculations of corrosivity ratios (CRs) indicated that the groundwater is unsuitable for industrial uses. Finally, a health risk assessment of iron heavy metal related to the hazard index (HI) for both ingestion and dermal exposure in children and adults showed negligible-to-low risk from iron exposure.

Keywords: massive dune aquifer, groundwater quality, principal component analysis, health risk assessment, hazard index, iron heavy metal.

INTRODUCTION

Groundwater is a valuable natural resource that is used not just for drinking but also for agricultural and industrial purposes [Zhang et al., 2018; Egbi et al., 2019]. Natural circumstances, industrial clusters, transportation and human activities have all contributed to a fast expansion in coastal populations, and demand for water resources has reached an all-time high [Wang et al., 2023]. Water resources are now seriously under threat, due to excessive water usage for irrigation and industrial purposes [Solangi et al.,

2019]. Therefore, increased demand has resulted in decreased groundwater quality in many regions of the world due to water shortages [Salameh et al., 2021]. At the same time, groundwater quality is also determined by several factors, including water type, rainfall quantity, recharged water quality, physicochemical composition, chemical degradation dependent on regional geology, rock weathering, residence period, seawater intrusion, seepage of polluted surface water, salinity, discharge of human pollutants and other human activities [Lima et al., 2019; Singh et al., 2022]. Consequently, prior to the use of groundwater for

various purposes, a water quality assessment is therefore required [Saha and Paul, 2019].

Water quality evaluation can be assessed using several techniques [Yin et al., 2021], including indexing methods, which are worldwide used. The most prevalent tool for assessing water quality for drinking or irrigation is the water quality index (WQI), because it considers the overall quality of water in a single computing system [Shil et al., 2019; Zhang et al., 2020; Azlaoui et al., 2021]. Furthermore, the health risk assessment via hazard index (HI) of water quality can also be useful in quantifying the potential risk to humans from water consumption or by skin contact [Bhutiani et al., 2016; Adimalla and Li, 2019]. Such assessment is based on the most commonly used model recommended by the United States Environmental Protection Agency (USEPA). In addition, indices such as the total dissolved solids (TDS), sodium absorption ratio (SAR), percentage of sodium (Na %), residual sodium carbonate (RSC), magnesium hazard (MH), Kelly index (KI), permeability index (PI) and irrigation water quality index (IWQI) are all used for evaluating irrigation-water suitability [Wang et al., 2023]. For industrial purposes, water quality may be assessed in terms of the corrosivity ratio (CR) [Patel et al., 2016]. Multivariate statistical approaches are also widely used and they include cluster analysis (CA), factor analysis (FA), principal component analysis (PCA) and discriminant analysis (DA) [Taşan et al., 2022].

The massive dune aquifer of Bouteldja has been studied by many researchers [Toubal, 1998; Assassi et al., 2004; Saaidia, 2008; Sebaïti, 2010; Haied et al., 2015; Haied, 2015; Sedrati et al., 2016; Aichouri, 2016; Bounab et al., 2017; Djoudar Hallal et al., 2019]. Saaidia [2008] and Sebaïti [2010] highlighted a decrease in its piezometric level using hydrodynamical simulation models at the Bordj Ali Bey and across the entire aquifer, respectively; these indicated overexploitation of the aquifer. Djoudar Hallal [2019] identified low-to-medium vulnerability of the aquifer to marine intrusion using the GALDIT method, while Sedrati [2016] reported a moderate-to-high level of vulnerability to pollution. In this study, we investigate possible deterioration of water quality based on the quality of the groundwater for drinking, irrigation and industrial uses. We also carried out a health risk assessment. The study objectives were as follows: (1) to identify the overall groundwater quality based on hydrochemical properties; (2) to assess the groundwater's suitability for drinking, irrigation, and industrial purposes; and (3) to evaluate the health risk presented by iron (Fe) to both children and adults.

STUDY AREA DESCRIPTION

Study area

The study area was located in El Tarf province between $7^{\circ}56'55''$ and $8^{\circ}17'43''$ east longitude; and between $36^{\circ}48'45''$ and $36^{\circ}56'13''$

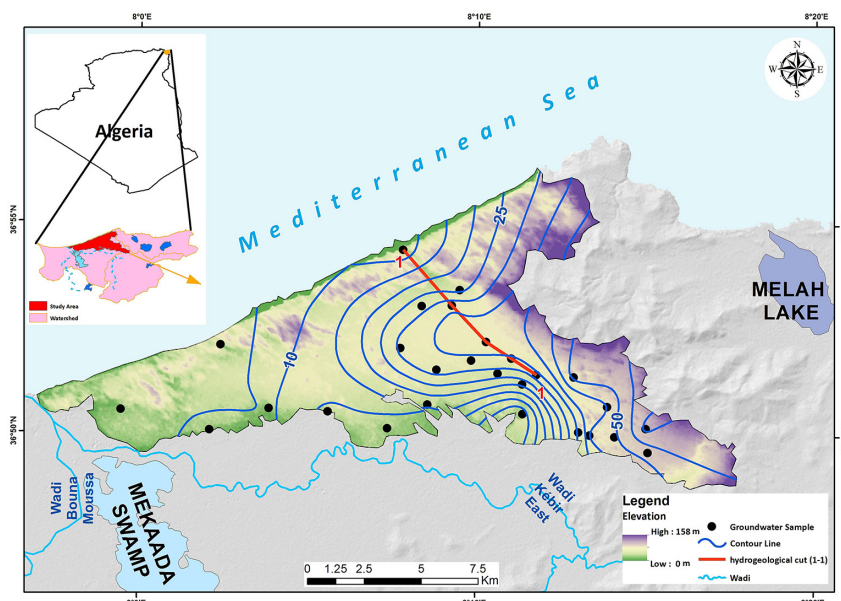


Figure 1. Geographical location and piezometric level of the massive dune aquifer

north latitude and comprised in El Mafragh watershed. The study area's average elevation is 79 meters with a total area of 164.28 km² (Figure 1). The aquifer is limited on the north by the Mediterranean Sea, on the south by the Bouteldja plain, on the east by the Rosa Cape, and on the west by the Wadi Mafragh. The region is subject to a Mediterranean type of climate and can be classified as a sub-humid zone. During the period 2011–2021, annual precipitation ranged between 397.30 mm and 814.82 mm, with average monthly temperatures rising from 16.83 °C in the winter to 31.67 °C in the summer.

Geology and hydrogeology

Many geological studies have previously been carried out in the study area [Joleaud, 1936; Hilly, 1962; Vila, 1980; Gleizes et al., 1988]; these have shown that the region is formed by metamorphic and sedimentary formations (Figure 2). The massive dune aquifer of Bouteldja mostly consists of quaternary sand with intercalations of clay (Figure 3). Because of the production of the massive dune aquifer boreholes, which has continued since their inauguration (except during the fires of 1994), the work of Khérici [1985] provided the

only available data on piezometric characteristics of the study area. Figure 1 shows that the underground flow is directed to the sea in the north and to the Wadi Kebir-East terraces in the south. Another flow can be identified in the southeast zone; this receives its supply of water by the flows coming from the sandstone-clayey reliefs. In this aquifer, the recharge occurs through rainfall infiltration, as well as by diffuse streams on the reliefs of Djebel Koursi [Haied et al., 2015].

MATERIALS AND METHODS

Data

Data were obtained from the Algerian Waters Central Laboratory. Twenty-five groundwater samples were collected in September 2019 in the unconfined massive dune aquifer of Bouteldja for analysis of sixteen physicochemical parameters (potential of hydrogen (pH), electrical conductivity (EC), total dissolved solids (TDS), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), chloride (Cl), bicarbonate (HCO₃), sulfate (SO₄), fluoride (F), nitrate (NO₃), ammonium (NH₄), orthophosphate

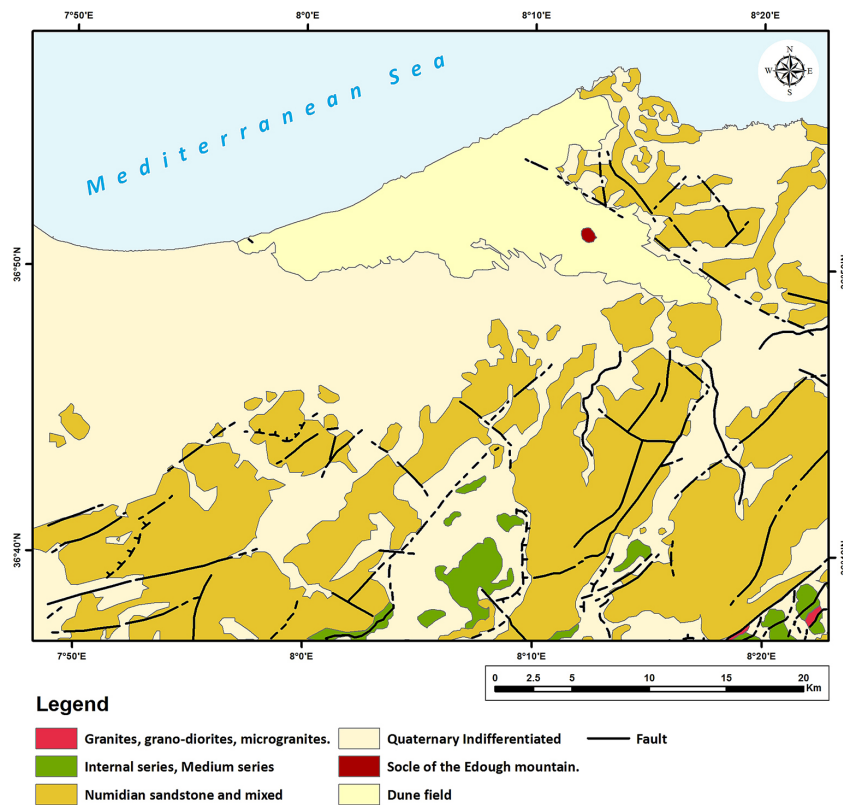


Figure 2. Geological map of the study area [Vila, 1980]

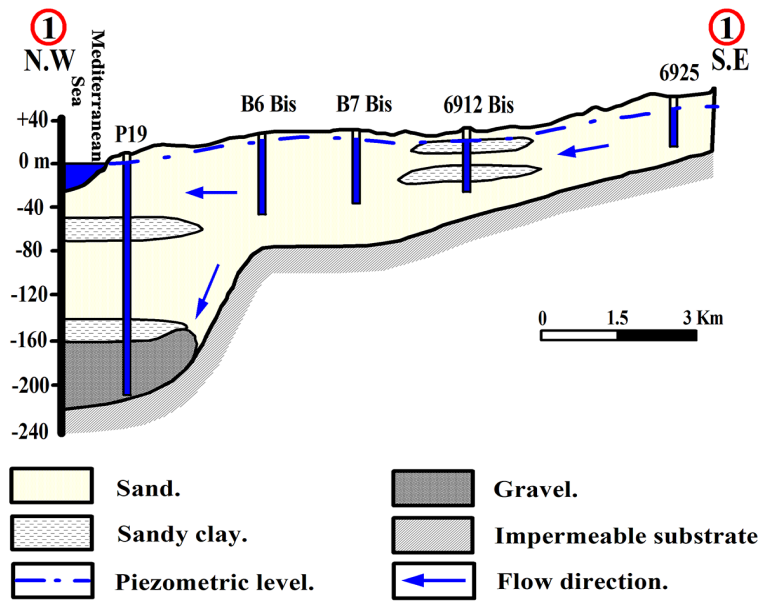


Figure 3. Hydrogeological cut (1–1) through the massive dune aquifer [Haied, 2015]

(PO_4), iron (Fe) and aluminum (Al)) (Figure 4). For this purpose, the geographical coordinates were validated on site and the samples were collected in pre-cleaned polythene bottles based on Rodier [1996] sampling methods. The potential of hydrogen (pH), EC and total dissolved solids (TDS) were measured in situ by using a portable multiparameter. Calcium, magnesium and total hardness (TH) were determined using the complexometry method with Ethylene Diamine Tetra-Acetic Acid (EDTA). The determination of the total alkalinity was carried out using the titration with HCl, sodium, potassium, iron and aluminum by flame atomic absorption spectrometry, the chloride by titration with potassium chromate. Finally, sulfate, fluoride, nitrate, ammonium and orthophosphate were measured

with a UV spectrophotometer. The evaluation of the analytical data and the statistical processing were carried out using XLSTAT software [Addinsoft, 2021].

Hydrochemical analysis

Among the most-used hydrogeochemical methods for surveying the evolution of groundwater quality and sources of groundwater recharge [Ye et al., 2022] is the Durov diagram [Durov, 1948] which enables the chemical composition of groundwater to be determined [Ahmed et al., 2020; Hui et al., 2021]. The spatial distribution maps were performed using the interpolation algorithm of Kriging and the Qgis 3.16 for the automatic mapping.

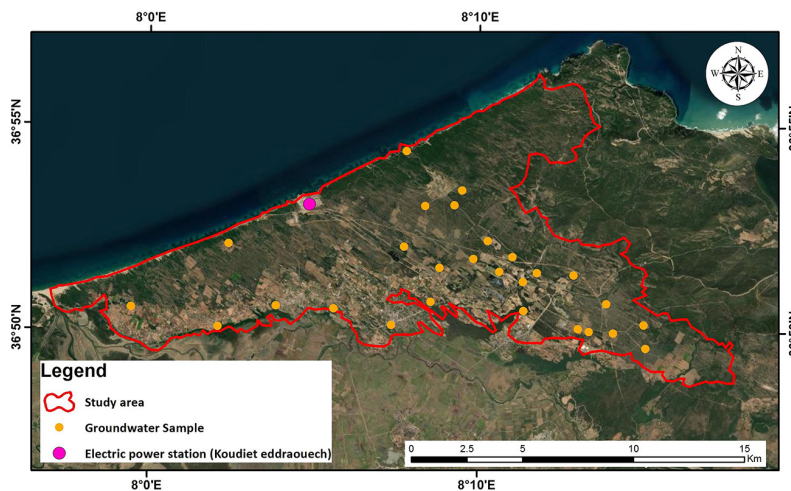


Figure 4. Groundwater sampling points distribution

Multivariate statistical analysis

In order to identify the variables influencing quality of groundwater and its suitability for several purposes, the multivariate statistical analysis is commonly performed using principal component analysis (PCA). Reimann and Filzmoser [2000] demonstrated that the direct application of PCA generally allows errors in the results due to the “closure effect”. Hence, the principal component analysis was conducted after transformation of raw data into centered log ratio (PCA-clr) as suggested by many authors [e.g., Ebrahimi et al., 2021; Ferhaoui et al., 2022] following the method of Aitchison [1986]. The CodaPack software [Comas-Cufi and Thió-Henestrosa, 2011] was used to conduct the clr-transformation.

Assessment of groundwater quality

Drinking use

The water quality index (WQI) was developed by Brown et al. [1970] for checking the suitability of water for drinking purposes based on World Health Organization (WHO) standards. It is a widely used approach today. Each chemical indicator is given a weight (w_i) in the first step based on how important it is for the overall quality of the water (Table 1). Equation (1) is used in the second phase to generate relative weights (W_i) for each chemical parameter. The third step

involves calculating a quality rating scale (q_i) using Equation (2). Finally, the WQI is determined as the weighted sum of the quality ratings of all parameters, using Equation (3):

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \tag{1}$$

$$q_i = \left(\frac{C_i}{S_i}\right) \times 100 \tag{2}$$

$$WQI = \sum W_i \times q_i \tag{3}$$

where: w_i and W_i – the weight and relative weight, respectively, of each parameter; $n=15$, because fifteen parameters were used in this study; q_i – the quality assessment scale; C_i – the concentration of each chemical parameter in mg/L; S_i – the standards of the WHO [2017].

Irrigation use

The following parameters were used to assess the hazard of groundwater to soil in this study: percentage of sodium; sodium adsorption ratio),

Table 1. Physicochemical parameters and their assigned weights and relative weights for the WQI computation

Chemical parameters	WHO Standards [2017]	Weight (w_i)	Relative weight (W_i)
pH	8.50	3	0.06
TDS (mg/L)	500	5	0.11
Ca (mg/L)	75	2	0.04
Mg (mg/L)	50	2	0.04
Na (mg/L)	200	3	0.06
K (mg/L)	12	1	0.02
Cl (mg/L)	250	3	0.06
HCO ₃ (mg/L)	120	2	0.04
SO ₄ (mg/L)	250	3	0.06
F (mg/L)	1.50	3	0.06
NO ₃ (mg/L)	50	5	0.11
NH ₄ (mg/L)	35	3	0.06
PO ₄ (mg/L)	5	3	0.06
Fe (mg/L)	0.30	5	0.11
Al (mg/L)	0.20	2	0.04
		$\Sigma w_i = 45$	$\Sigma W_i = 1.00$

magnesium hazard; permeability index; and Kelly index. Added to these factors irrigation water quality index was also determined.

Sodium adsorption ratio

The sodium adsorption ratio (SAR) indicates high concentrations of calcium and magnesium, which can affect soil properties and cause decreased permeability [Batarseh et al., 2021]. The ratio is calculated as follows:

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}} \quad (4)$$

Percentage of sodium

High concentrations of Na in irrigation water are exchanged in soil for Ca and Mg, which reduce its permeability [Gaagai et al., 2023]. The sodium percentage is calculated as follows:

$$Na \% = \frac{(Na + K) * 100}{(Ca + Mg + Na + K)} \quad (5)$$

Magnesium hazard

High concentrations of Mg ion in water can increase soil alkalinity, leading to lower levels of crop production. Magnesium hazard (MH) is calculated as follows:

$$MH = \frac{(Mg * 100)}{(Ca + Mg)} \quad (6)$$

Kelly index

Developed by Kelly [1963], this index is based on Na, Ca and Mg concentrations in water. Irrigation water is considered unsuitable if KI is higher than 1. It is calculated using the Equation (7):

$$KI = \frac{Na}{Ca + Mg} \quad (7)$$

Permeability index

Proposed by Doneen [1964], the permeability index is based on Na, Ca, Mg, and HCO_3 levels, and is calculated using Equation (8), as follows:

$$PI = \frac{(Na + \sqrt{HCO_3}) * 100}{(Ca + Mg + Na)} \quad (8)$$

Irrigation water quality index

The IWQI was developed by Meireles et al. [2010] and is used to measure water quality in agricultural applications [Meireles et al., 2010; Abbasnia et al., 2018]. It is based on the EC, Na, Cl, HCO_3 , and SAR as described in Equation (9):

$$IWQI = \sum_{i=1}^n q_i \cdot w_i \quad (9)$$

where: q_i – the water quality measurement parameter is determined by the equation (10):

$$q_i = q_{max} - \left(\frac{[(x_{ij} - x_{inf})q_{iamp}]}{x_{amp}} \right) \quad (10)$$

where: q_{max} – the class’s highest value of q_i ;
 x_{ij} – the parameter concentration;
 x_{inf} – the class’s minimum value of each indicator;
 q_{iamp} and x_{map} – the class’s amplitude of q_i and the indicator, respectively; Table 2 depicts the estimation of the q_i value;
 w_i – the accumulated weights which is determined based on the relative significance and values of the agricultural water quality (Table 3).

Industrial use

The corrosivity ratio (CR) is the ratio of alkaline earths to saline salts in groundwater. It is used to determine the sensitivity of groundwater to corrosion, which may result in the decreased hydraulic capacity of pipes. Water samples with CR values greater than 1

Table 2. Limiting values of parameter for q_i and the proposed indicators for calculating IWQI [Meireles et al., 2010]

q_i	EC ($\mu\text{s}/\text{cm}$)	Na (meq/L)	Cl (meq/L)	HCO_3 (meq/L)	SAR (meq/L) ^{1/2}
85–100	$0.20 \leq \text{EC} < 0.75$	$2.00 \leq \text{Na} < 3.00$	$1.00 \leq \text{Cl} < 4.00$	$1.00 \leq \text{HCO}_3 < 1.50$	$2.00 \leq \text{SAR} < 3.00$
60–85	$0.75 \leq \text{EC} < 1.50$	$3.00 \leq \text{Na} < 6.00$	$4.00 \leq \text{Cl} < 7.00$	$1.50 \leq \text{HCO}_3 < 4.50$	$3.00 \leq \text{SAR} < 6.00$
35–60	$1.50 \leq \text{EC} < 3.00$	$6.00 \leq \text{Na} < 12.00$	$7.00 \leq \text{Cl} < 10.00$	$4.50 \leq \text{HCO}_3 < 8.50$	$6.00 \leq \text{SAR} < 12.00$
0–35	$\text{EC} < 0.20$ or $\text{EC} \geq 3.00$	$\text{Na} < 2.00$ or $\text{Na} \geq 12.00$	$\text{Cl} < 1.00$ or $\text{Cl} \geq 10.00$	$\text{HCO}_3 < 1.00$ or $\text{HCO}_3 \geq 8.50$	$\text{SAR} < 2.00$ or $\text{SAR} \geq 12.00$

Table 3. IWQI indicators weights [Meireles et al., 2010].

Indicator	w_i
EC	0.211
Na	0.204
HCO_3	0.202
Cl	0.194
SAR	0.189
Total	1.000

EF – the exposure frequency;
ED – the exposure duration;
BW – the body weight;
AT – the average time;
SA – the exposed skin area;
AF – the adherence factor;
ABSd – the dermal absorption fraction;
ET – the exposure time;
CF – the conversion factor (Table 4).

($\text{CR} > 1$) are considered unsuitable for industrial use [Patel et al., 2016; Saha et al., 2019; Selvam et al., 2021].

$$\text{HQ} = \frac{\text{CDI (ingestion or dermal)}}{\text{RFD (ingestion or dermal)}} \quad (13)$$

Health risk assessment

Chronic daily intake

Human exposure to heavy metals either through ingestion (water consumption) or dermally (skin exposure) can be evaluated using the chronic daily intake (CDI) for children and adults based on the United States Environmental Protection Agency (USEPA) [Selvam et al., 2021; Gad et al., 2023]. The hazard quotient (HQ) can be derived by dividing the CDI by the reference dose (RFD) using Equations (11, 12 and 13) as follows:

$$\text{CDI Ingestion} = \frac{\text{MC} * \text{ingR} * \text{EF} * \text{ED}}{\text{BW} * \text{AT}} \quad (11)$$

$$\text{CDI Dermal} = \frac{\text{MC} * \text{SA} * \text{AF} * \text{ABSd} * \text{ET} * \text{EF} * \text{ED} * \text{CF}}{\text{BW} * \text{AT}} \quad (12)$$

where: *MC* – the element concentration (mg/L);
ingR – the ingestion rate;

Hazard Index (HI) can be calculated by summing the HQ values for each detected heavy metal.

$$\text{HI} = \sum \text{HQ}_i \quad (14)$$

Table 4. Factors influencing chronic daily intake and health indices [Gad et al., 2023]

Factors	Fe	
	Children	Adult
Ingestion rate (IngR)	0.78 L/day	2.50 L/day
Exposure frequency (EF)	350 days/year	
Exposure duration (ED)	6 years	30 years
Body weight (BW)	15 kg	52 kg
Average time (AT)	2190 days	10950 days
Exposed skin area (SA)	0.66 m ²	1.80 m ²
Adherence factor (AF)	0.07	
Dermal absorption fraction (ABSd)	0.03	
Exposure time (ET)	0.58 h/day	
Conversion factor (CF)	10 ⁻² kg/mg	
Ingestion reference dose (RFD)	0.70	
Dermal reference dose (RFD)	0.14	

RESULT AND DISCUSSIONS

Groundwater characterization

The WHO guidelines were used to evaluate the physicochemical properties (Table 1). Water used for drinking purposes should have a pH value between 6.50 and 8.50. In the studied samples, pH values ranged from 5.56 to 7.86. The average pH value of groundwater samples in the study area was 6.71. Of the 25 samples, 21 samples were characterized by a pH value below the WHO limits. These results implied that the groundwater in the study area was slightly-acidic-to-alkaline.

The main criterion used to evaluate water quality for varied uses is electrical conductivity

(EC). Its values ranged from 120 to 329 $\mu\text{S}/\text{cm}$. Overall, the analyzed water samples yield EC values lower than the WHO standards. As water samples evaporate, the amount of salts left behind can be expressed as total dissolved solids (TDS) [Solangi et al., 2019]. TDS levels in samples ranged from 87.00 mg/L to 221.00 mg/L (Table 5). We found that TDS concentrations were lower than the WHO standard of 500 mg/L. Based on TDS and EC, groundwater can be classified as shown in Table 6. Subsequently, and as set out in Table 6 and Figure 5, we determined that 96.15 % of samples were either excellent (84.61%) or good (11.53%) for drinking based on EC. Accordingly, the TDS showed that 96.15% of samples were suitable for drinking purposes.

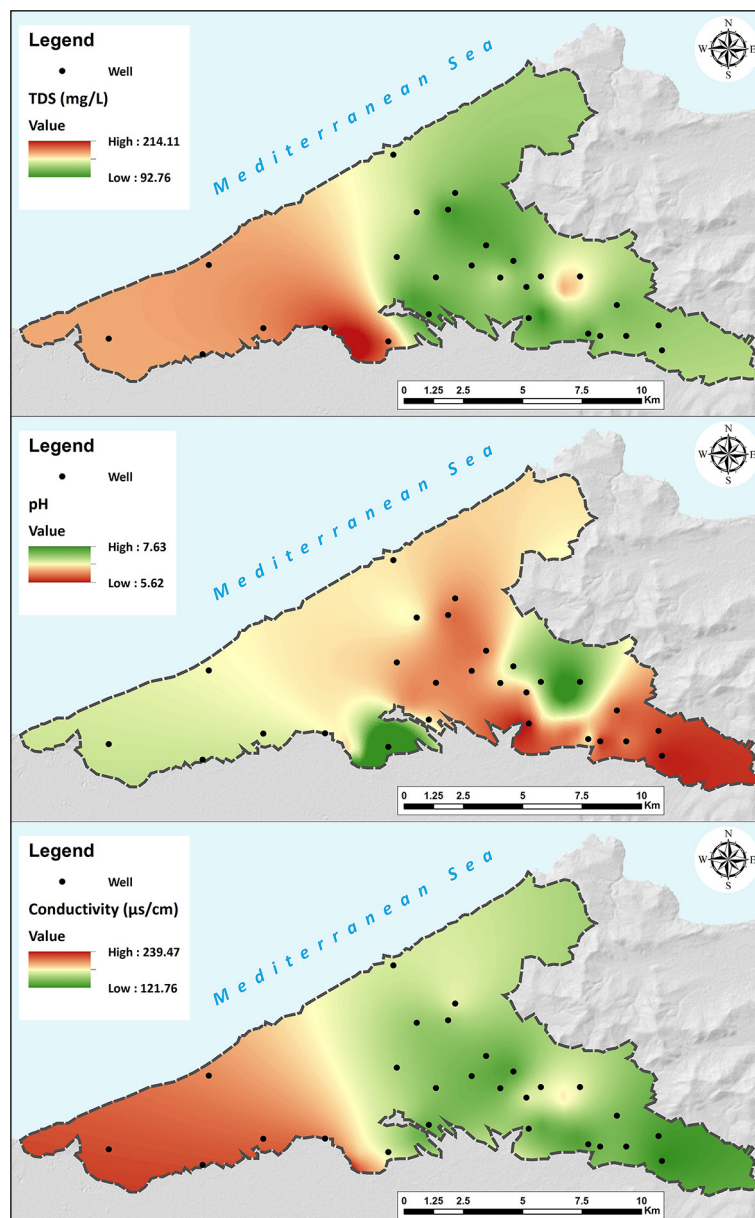


Figure 5. Spatial map of the distribution level of the TDS, pH and CE in the study area

As shown by Table 5 and Figure 6, sodium and potassium were the dominant anions along with calcium, with an average of 26.00 mg/L, 2.76 mg/L, and 6.67 mg/L, respectively. The main dominant anion was chloride with an average of 34.13 mg/L followed by the bicarbonates with an average of 27.52 mg/L. The sulfate and nitrate have a concentrations average of 17.48 mg/L and 7.05 mg/L, respectively. Hence, the order of cation and anion concentrations was $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$, $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$.

Durov diagram

Based on the Durov diagram (Figure 7), which was used to correctly reflect and describe the groundwater chemistry in the study area [Karunanidhi et al., 2019]. The water samples were plotted mainly into the fields 3 and 6 as shown by Figure 6. Based on the classification of Lloyd and Heathcoat [1985], the fields 3 and 6 indicate that water ions reflect a mixing of freshwater, with an influence of the sea position near the aquifer and

cation exchange. Fields 2 and 5 in which some water samples were plotted (6 water samples: 4 samples into the field 2 and 2 samples plotted into the field 5) indicating a reverse cation exchange and mixing reactions from various origins.

Multivariate statistical analysis

Correlation matrix analysis

Major-ion concentrations and correlation matrices were used to determine chemical processes [Kechiched et al., 2020; Sako and Kafando, 2021; Imbulana et al., 2021]. A Pearson’s correlation matrix on clr-data revealed very strong positive correlation between most major ions Na, K, Cl, SO_4 and F and their very strong negative correlation with Fe (Table 7). These high correlations could be explained by ions sharing a similar source [El-Rawy et al., 2023]. Other thermodynamic equilibrium origins could explain the low and non-significant correlations.

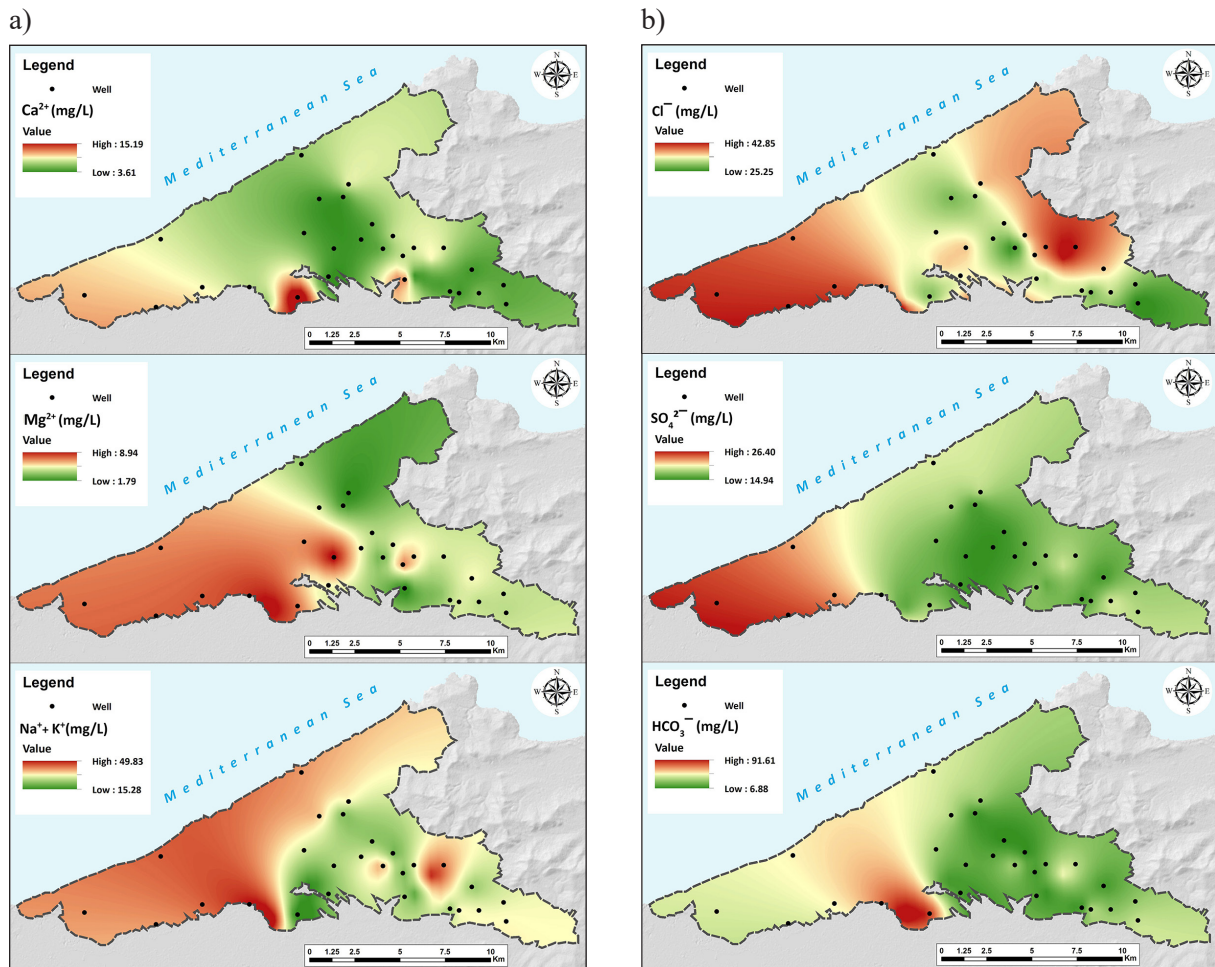


Figure 6. Spatial distribution maps of the major ions

Table 5. Descriptive statistics of the investigated physicochemical parameters

Parameters	Unit	Minimum	Maximum	Mean	Standard deviation
pH	-	5.56	7.86	6.18	0.54
CE	μS/cm	2.29	329.00	160.16	61.76
TDS	mg/L	87.00	221.00	128.96	35.22
Ca	mg/L	3.21	32.86	7.11	5.95
Mg	mg/L	1.46	9.23	5.01	2.23
Na	mg/L	11.72	47.00	25.84	9.19
K	mg/L	2.63	3.00	2.95	0.11
Cl	mg/L	24.82	49.63	34.13	6.11
SO ₄	mg/L	18.34	20.00	20.21	1.83
HCO ₃	mg/L	4.88	69.05	27.61	24.56
F	mg/L	0.08	0.26	0.12	0.04
NO ₃	mg/L	2.20	14.54	9.50	3.74
NH ₄	mg/L	0.00	0.13	0.05	0.03
PO ₄	mg/L	0.03	0.18	0.06	0.03
Fe	mg/L	0.01	7.40	1.34	2.12
Al	mg/L	0.01	0.08	0.03	0.01

Table 6. Groundwater classification according to TDS and EC [Baloch et al., 2023]

Parameters	Range	Water quality	Number of samples (%)
Electrical conductivity (EC) (μS/cm)	<250	Excellent	22 (84.61%)
	250–750	Good	3 (11.53%)
	750–2000	Permissible	0 (0.00%)
	2000–3000	Doubtful	0 (0.00%)
	>5000	Very hazardous	1 (3.84%)
Total dissolved solids (TDS) (mg/L)	<500	Desirable for drinking	25 (96.15%)
	500–1000	Acceptable for drinking	0 (0.00%)
	1000–3000	Suitable for irrigation	0 (0.00%)
	>3000	Hazardous for both	0 (0.00%)
			1 (3.84%)

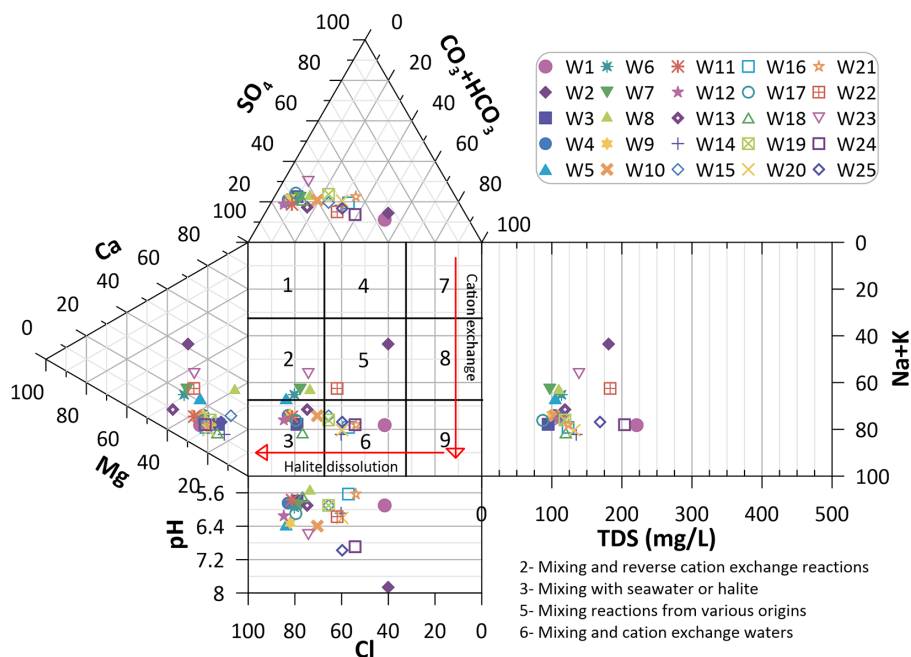


Figure 7. Durov diagram for the groundwater hydrochemical composition

Principal component analyses (PCA)

Thirteen variables were used in extracting main components after clr-transformation. The main two principal components (PCs) with 50.47% of cumulative variance were retained (Figure 8). The high factor loading in Factor 1 of Na, K, Cl, SO₄, Fe and F may be explained with reference to four processes including high evaporation; irrigation return flow; seawater intrusion; and cation exchange related to seawater intrusion [El-Rawy et al., 2023]. However, the latter two of these processes were excluded by Djoudar Halal [2019]. A positive load factor on Ca, HCO₃, NO₃ and NH₄ was observed in Factor 2. Of these, Ca and HCO₃ indicate groundwater alkalinity [El-Rawy et al., 2023], while NO₃ and NH₄ are related to an anaerobic and reducing environment, and to anthropogenic activities [Ye et al., 2022].

Assessment of groundwater quality

Drinking use

WQI values range between 12.50 and 294.63, averaging the value of 45.40. On the basis of our results, water quality may be classified into four classes (Figure 9). Among the twenty-five groundwater samples, twenty (80.00%) were classified as being of excellent quality, two (8.00%) were of good quality, one (4.00%) was of poor quality, and two (8.00%) were of very poor quality. The highest WQI values were obtained from samples with high concentrations of iron (W2, W10 and W15).

The WQI spatial distribution map (Figure 9) showed that the greatest deterioration in groundwater quality was recorded in the north-east, and south parts of the aquifer. The other parts, where the majority of sampling wells were located, were characterized by a good-to-excellent water classification.

Irrigation use

This study employed six indicators to assess the acceptability of groundwater for irrigation purposes, which is largely influenced by the amount of undesirable dissolved salts or

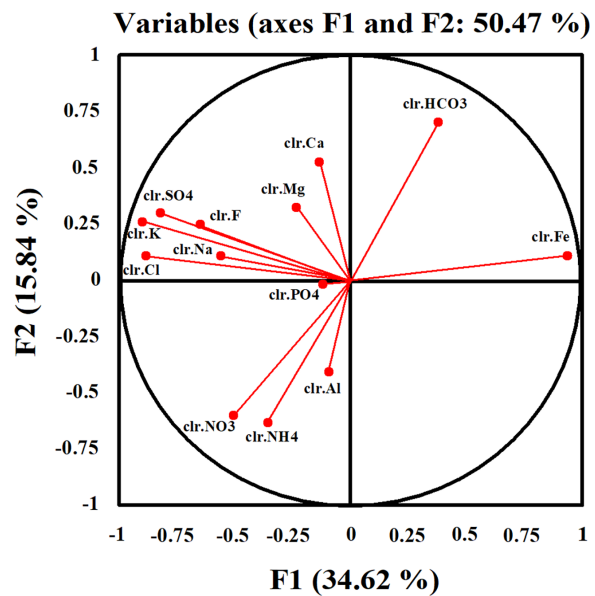


Figure 8. Centered log ratio principal component analysis (PCA-clr) of the hydrochemical parameters

Table 7. Pearson correlation matrix of hydrochemical parameters

Variables	Na	Ca	Mg	K	Cl	SO ₄	HCO ₃	NO ₃	Fe	NH ₄	PO ₄	F	Al
Na	1.00												
Ca	-0.22	1.00											
Mg	0.06	-0.04	1.00										
K	0.59	0.12	0.15	1.00									
Cl	0.47	0.22	0.35	0.75	1.00								
SO ₄	0.42	0.32	0.15	0.87	0.77	1.00							
HCO ₃	0.24	0.10	0.05	-0.10	-0.35	-0.21	1.00						
NO ₃	0.18	-0.17	-0.04	0.23	0.28	0.09	-0.53	1.00					
Fe	-0.60	-0.09	-0.22	-0.77	-0.76	-0.63	0.29	-0.61	1.00				
NH ₄	0.38	-0.33	-0.24	0.20	0.22	0.13	-0.43	0.37	-0.43	1.00			
PO ₄	-0.01	-0.09	0.04	0.04	0.02	-0.08	-0.07	0.13	-0.18	-0.19	1.00		
F	0.01	0.32	0.17	0.63	0.46	0.50	-0.20	0.34	-0.57	-0.10	0.33	1.00	
Al	-0.27	0.05	0.001	-0.07	0.14	0.04	-0.50	0.18	-0.15	-0.07	0.03	-0.04	1.00

Table 8. Groundwater quality classification

WQI range	Water type
<50	Excellent water
50–100.10	Good water
100–200.10	Poor water
200–300.10	Very poor water
>300	Unfit for drinking

compounds [El-Amier et al., 2021]; six indices were used in this study: SAR, Na %, MH, KI, PI and IWQI.

Sodium adsorption ratio

According to the calculated values for the groundwater samples, the SAR ranged from 0.85 to 4.24, with an average of 2.70. Results were plotted in the USSSL diagram [Richards, 1954]. Based on the SAR classification according to Richards (Figure 10a), 88.00% of total groundwater samples fall into the C1S1 category and 12.00% are found into the C2S1 category. These two results indicated that the groundwater of the study area was excellent-to-good for irrigation purposes.

Sodium percentage

The percentage of sodium (Na%) of the groundwater samples of the massive dune aquifer varied between 28.63% (at W2) and 76.24% (at W14), with an average of 61.27%. According to Na% values, 4.00% of the groundwater samples are good for irrigation, 24.00% are permissible for irrigation and 72.00% are of doubtful quality (Table 9). Higher percentages of Na exceeding 60% may result in sodium accumulations leading to alterations in the physical properties of soil [Fipps, 2003]. Contrarily, the Wilcox diagram [Wilcox,

1955], which is based on the relationship between Na % and EC, revealed that the groundwater may be classified as excellent (Figure 10b).

Magnesium hazards

The magnesium hazard (MH) computation values ranged between 16.69% and 79.15%, with an average of 56.41%. Approximately 76.00% of the groundwater samples in the aquifer were unsuitable for the purpose of irrigation; consequently, 24.00% of samples were suitable for this purpose (Table 9).

Kelly index

The KIs of groundwater samples spanned the range of 0.35 to 3.06, with an average value of 1.65. Accordingly, 80.00% of the groundwater samples surpassed the limit value (>1) and were therefore considered unsuitable for irrigation purposes (Table 9), probably owing to an excess of Na⁺ resulting from strong cation exchange [El-Amier et al., 2021; Xu et al., 2019].

Permeability index

The computed PI values ranged from 63.18% to 113.14%, with an average of 91.47%. We found that 88.00% of the groundwater samples were in class I (suitable for irrigation); the remainder (12.00%) belonged to class II (moderate quality for irrigation) (Table 9).

Irrigation water quality index

IWQI values were categorized as follows: only plants that can tolerate high levels of salt may be watered using groundwater in 4.00% of

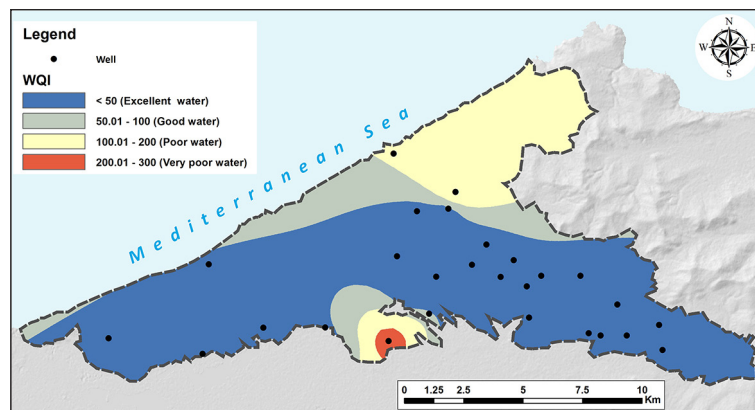


Figure 9. WQI spatial distribution map in the massive dune aquifer

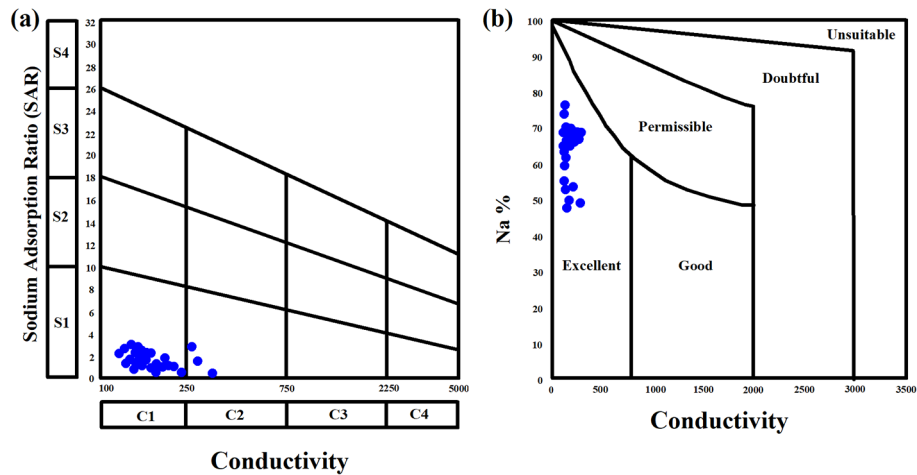


Figure 10. Groundwater suitability for irrigation assessment using (a) USSL and (b) Wilcox diagrams

the examined wells, preventing irrigation under typical circumstances. When examining the frequency of irrigation throughout the summer, it should be taken into account that 76.00% of the analyzed wells were classified as having a high restriction, which limits the use of irrigation water for moderate to high tolerance plants in permeable soil without compact layers. Note that 8.00% falls within the moderate restriction, which limits the use of irrigation groundwater for plants with moderate tolerance and recommends using wells in moderate to extremely permeable soil while accounting for moderate soil leaching processes. The low restriction category, which recommends avoiding irrigation of salt-sensitive plants and taking into account concerns with irrigated soil texture, permeability, and soil sodicity, was given to just 4.00% of the total number of wells. Finally, Table 9 shows that two wells (8.0%) were found to have no restriction category. Figure 11 showed clearly that the total area of the studied

region is classified into two parts: the east part, containing the majority of the wells, characterized by high-to-severe restriction categories, and the west part belonging to the moderate-to-no restriction categories.

Industrial use

The corrosivity ratio (CR) computation allowed showing that the values in the study area are ranging between 0.72 and 14.15. Only two sampling points representing 8.00% of total points were characterized by appropriate water for industrial uses (W1 and W2).

Health risk assessment indices

Chronic daily intake

The chronic daily intake (CDI), hazard quotient, and hazard index were used to assess potential health concerns associated with heavy metal exposure in both adults and children. Considering CDI Ingestion and CDI Dermal

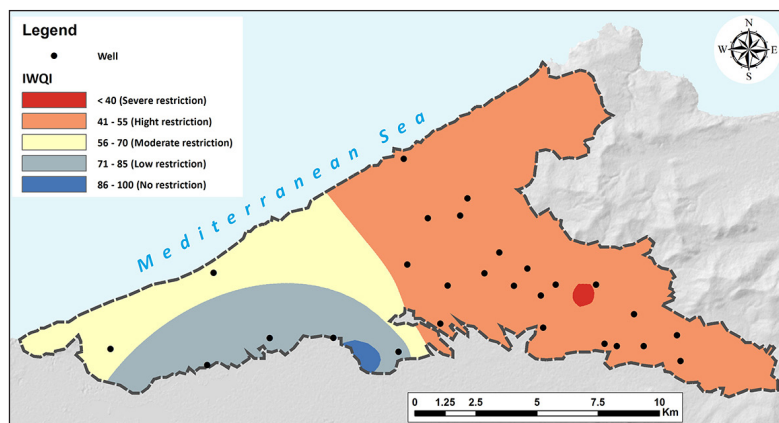


Figure 11. Spatial distribution map of the IWQI classes in the massive dune aquifer

Table 9. Classification thresholds of groundwater quality indices for irrigation purposes

Indices	Range	Water quality	Number of samples (%)	References
SAR	<10	Excellent	25 (100.00%)	[Richards, 1954]
	10–18	Good	0 (0.00%)	
	19–26	Doubtful	0 (0.00%)	
	>26	Unsuitable	0 (0.00%)	
Na %	<20%	Excellent	0 (0.00%)	[Wilcox, 1955]
	21–40%	Good	1 (4.00%)	
	41–60%	Permissible	6 (24.00%)	
	61–80%	Doubtful	18 (72.00%)	
	>80%	Unsuitable	0 (0.00%)	
MH	>50%	Suitable	6 (24.00%)	[Paliwal, 1972]
	<50%	Unsuitable	19 (76.00%)	
KI	<1	Suitable	5 (20.00%)	[Kelly, 1963]
	>1	Unsuitable	20 (80.00%)	
PI	>75%	Suitable	22 (88.00%)	[Doneen, 1964]
	25–75%	Moderate	3 (12.00%)	
	<25%	Unsuitable	0 (0.00%)	
IWQI	85–100	no restriction	2 (8.00%)	[Meiros, 2010]
	70–85	low restriction	1 (4.00%)	
	55–70	moderate restriction	2 (8.00%)	
	40–55	high restriction	19 (76.00%)	
	0–40	severe restriction	1 (4.00%)	

values for both age groups with respect to Fe (Table 10), we found that values for CDI Ingestion were higher than those for CDI Dermal, although both of values are within acceptable limits (<1) with averages of $4.03 \times 10^{-2} \text{ mg L}^{-1} \text{ day}^{-1}$ and $7.16 \times 10^{-7} \text{ mg L}^{-1} \text{ day}^{-1}$ for children and $3.72 \times 10^{-2} \text{ mg L}^{-1} \text{ day}^{-1}$ and $5.63 \times 10^{-7} \text{ mg L}^{-1} \text{ day}^{-1}$ for adults, for CDI Ingestion and CDI Dermal, respectively (Table 10). We therefore concluded that exposure to Fe in the study area does not endanger human health. Similarly to CDI, HQ showed low-to-negligible ingestion risk and low dermal risk for both children and adults (Table 11). However, HQ Ingestion

values were higher than those of HQ Dermal. For HQ Ingestion, mean values were 5.75×10^{-2} for children and 5.32×10^{-2} for adults; for HQ Dermal, mean values were 5.11×10^{-6} for children and 4.02×10^{-6} for adults (Table 10). It should be noted that because the HI is the sum of HQ values for each metal, and because only one metal was detected in the study area (Fe), the HI and HQ values are identical.

Even though the groundwater contained some Fe values exceeding the allowable concentration, both ingestion and dermal HI values indicated a negligible-to-low level of risk from exposure to iron (Fe) heavy metal (Table 11).

Table 10. Statistical analyses for Chronic daily intake (CDI) and hazard quotient (HQ)

Heavy metal	Parameter	Group	Minimum		Maximum		Mean	
			Ingestion	Dermal	Ingestion	Dermal	Ingestion	Dermal
Iron (Fe)	CDI ($\text{mg L}^{-1} \text{ day}^{-1}$)	Children	$4.99 \cdot 10^{-4}$	$8.86 \cdot 10^{-9}$	$3.68 \cdot 10^{-1}$	$6.55 \cdot 10^{-6}$	$4.03 \cdot 10^{-2}$	$7.16 \cdot 10^{-7}$
		Adults	$4.61 \cdot 10^{-4}$	$6.97 \cdot 10^{-9}$	$3.41 \cdot 10^{-1}$	$5.15 \cdot 10^{-6}$	$3.72 \cdot 10^{-2}$	$5.63 \cdot 10^{-7}$
	HQ	Children	$7.12 \cdot 10^{-4}$	$6.32 \cdot 10^{-8}$	$5.27 \cdot 10^{-1}$	$4.68 \cdot 10^{-5}$	$5.75 \cdot 10^{-2}$	$5.11 \cdot 10^{-6}$
		Adults	$6.58 \cdot 10^{-4}$	$4.97 \cdot 10^{-8}$	$4.87 \cdot 10^{-1}$	$3.68 \cdot 10^{-5}$	$5.32 \cdot 10^{-2}$	$4.02 \cdot 10^{-6}$

Table 11. Chronic risk classification [Baloch et al., 2023]

Heavy metal	Group	Hazard quotient (HQ ingestion and dermal)	Range	Samples number	
				HQ ingestion	HQ dermal
Iron (Fe)	Children	<0.1	Negligible	22	25
		$\geq 0.1 < 1$	Low	03	None
		$\geq 1 < 4$	Medium	None	None
		≥ 4	High	None	None
	Adults	<0.1	Negligible	22	25
		$\geq 0.1 < 1$	Low	03	None
		$\geq 1 < 4$	Medium	None	None
		≥ 4	High	None	None

CONCLUSIONS

This study aimed to assess groundwater quality using hydrochemical methods: the water quality index for drinking suitability; the sodium absorption coefficient, sodium percentage, magnesium hazard, Kelly index, permeability index and irrigation water quality index for irrigation purposes; and the corrosivity ratio for industrial uses. We also assessed the potential health risk posed by iron. Through the physicochemical analysis data, major ion concentrations were reported as follows: $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ for the cations and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$ for the anions. A Durov diagram revealed the water ions reflect a mixing of freshwater, with an influence of the sea position near the aquifer and cation exchange. Furthermore, the statistical analysis based on Pearson's correlation matrix and principal component analysis after a transformation into centred log ratio data show strong correlation between Na, K, Cl, SO_4 , Fe and F, which could be indicative to their similar origin from ion exchange and the proximity of the sea. The WQI values computed for the 25 samples varied between 12.50 and 294.63 revealing a predominance of excellent-quality water (80.00%) and good-quality water (8.00%), which was distributed over most parts of the aquifer where the majority of water samples were obtained. The sodium percentage, magnesium hazard, Kelly index and irrigation water quality index were determined to be with an average of 61.27%, 56.41%, 1.65, and 51.70, respectively. All these indices categorized the majority of sampled points as unsuitable for irrigation; however, the sodium adsorption ratio, Richards and Wilcox diagrams, and the permeability index revealed that they are suitable for this purpose. The corrosivity ratio categorized the majority of the massive dune aquifer of Bouteldja as unsuitable for industrial uses. Even though some water samples of massive dune aquifer contained high levels of the heavy metal Fe (0.01–7.40 mg/L), with concentrations exceeding the allowable limits recommended by the WHO, the ingestion and dermal hazard index values for children and adults both showed negligible-to-low risk from exposure to this heavy metal.

Based on these findings, some perspectives and recommendations can be summarized in order to properly manage water resources of the study region. Groundwater in the study area should be used exclusively for drinking

purposes, with restrictions for agricultural and industrial uses. Community awareness about limiting groundwater waste and overuse through sustainable policies and practices in order to avoid groundwater resources pollution and ensuring regular groundwater quality monitoring for detecting potential pollution. Once adopted by decision-makers and groundwater managers, these perspectives and recommendations can improve groundwater management of the study area. The present study is limited to the hydrochemical study of groundwater. Hydrogeochemical studies based on trace elements and isotopes may be undertaken in the future.

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