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ORIGINAL ARTICLE

Hydrogeochemical processes and multivariate analysis for groundwater quality in the arid Maadher region of Hodna, northern Algeria

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Abstract This study focused on water quality and hydrogeochemical processes (evolution, origin) in the Maadher region, central Hodna in Algeria. In recent decades, the excessive exploitation of this resource due to urbanization, irrigation, and the effect of climate change reaching the countries of northern Africa have caused a decline in water levels and hydrochemical changes in the aquifer. The sampling campaign in 2019 based on 13 physicochemical parameters was carried out on the water from 32 boreholes in the study area, compared to data archives of both sampling campaigns in 1967 and 1996. The result revealed that the groundwater as a whole has moderate freshwater quality, due to its total dissolved solids (TDS) content and other dissolved ions of concern (nitrate NO_3^-), which exceed WHO standards. In addition, Piper diagram indicates that the hydrochemical facies of sulfate–chloride–nitrate–calcium (SO_4^{2-}–Cl^-–NO_3^-–Ca^{2+} type), which globally characterizes the study area and these elements are the dominant dissolved ions. Principal component analysis and hierarchical cluster analysis (HCA) methodologies are applied in order to define the major control factors that affect the hydrochemistry of Maadher plain. Three distinct water groups were found, illustrating a different evolution of salinity (EC and TDS). The HCA indicated an interesting cluster with a distinct contamination signature and most likely with significantly higher sulfate, chloride, and nitrate concentrations. Anthropogenic processes also play an important role in the study area. The water resource comes from Bousaada Wadi, the exchange at the aquifer depth and the agricultural practices contribute to the deterioration of the quality.

Keywords Groundwater quality · Hydrogeochemical processes · Multivariate analysis · Salinity · Mio-Plio-Quaternary aquifer

1 Introduction

In the Algerian arid region, the Hodna basin is marked by a wide-open depression of 8500 km^2 surrounded by mountains, where the saltwater lake “Chott Hodna” is located in the center. Two exploitable shallow and deep aquifers exist in this region for domestic and irrigation use for 60 years, and hence, excessive overexploitation began to occur in this region (Benabderrahmane 1988). Especially, the water level in the shallow aquifer is dropping sharply inducing a significantly high salt concentration (ANRH 2007). On the other hand, the deep aquifer with relatively low salt concentration is the main source of water in the region (Guiraud 1970). Water with good quality and sufficient quantity from different resources is a backbone for the economic development of a region. The demand for water has increased rapidly with urbanization, irrigated agriculture and industrial developments. In Hodna basin, particularly in the densely populated Bousaada region, the main sources of water supply for drinking and irrigation activities are provided by the Maadher aquifer, and the water supply comes from pumped boreholes. In recent years, the groundwater of the Maadher aquifer has been threatened by several anthropogenic factors. Land-use change for

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urbanization and agricultural activities commonly results in the deterioration of water quality.

Water quality issues in the area are of great concern, and research on hydro-geochemical studies is limited. As a result, the hydro-geochemical processes (evolution), the origins, and the quality of the water resource in the Maadher region are poorly known. In addition, the origin of water quality parameters and the appearance of pollution (Abdesselam et al. 2013; Benabderrahmane 1988) have led to uncertainty in the understanding of the main hydro-geochemical processes that control water chemistry and which can considerably change the methods of drinking water treatment.

It is necessary to analyze and interpret water quality parameters of groundwater samples data, and also to determine hydrochemical water types (Dalton and Upchurch 1978), to evaluate water quality criteria (drinking) with hydro-geochemical processes (dissolution of minerals, ion exchange reaction, pollution of water) (Verma and Singh 2021; Mir and Gani 2019). Moreover, the impact of geology and land use on groundwater quality was presented in Maadher region.

Since the 1970s, the Hodna basin has experienced remarkable climatic changes (Ouhamdouch et al. 2019; Boudiaf et al. 2020); reduced and erratic rainfall was recorded, besides a noticeable increase in temperature. In addition, the large increase in population (estimated at over 184,694 in 2017) with the growth of these agricultural activities has been granted with the massive pumping of groundwater (ANRH 2007). The large volume of pumped water has contributed to the drop in water level and very possible the appearance of geochemical imbalance of the aquifer in the region.

The quality of groundwater in the region is largely influenced both by natural processes (lithology), state of recharge water resources (wadis, interaction with other types of deep aquifers) and by anthropogenic factors (agricultural activities, races of wastewater with water resources of the wadi), and also by aquifer overexploitation (Pophare et al. 2014). Water quality data and periodic water quality monitoring can provide information on the effects of increasing development and climate change on the environment (Nyagumbo et al. 2019). Hence, this study was carried out to identify the hydrochemical processes that control water chemistry and the origin of quality parameters in the Maadher region. It is believed that the results of this work will provide decision-makers in the public sector with better information on the quality situation of groundwater in the region.

The methodology designed for this research work includes five main phases: laboratory analysis, verification of results, statistical methods, water quality assessments and rock/water interaction.

2 Materials and methods

2.1 Study area

The Maadher region is in the central part of the Hodna basin and is 260 km south of Algiers. The plain of Maadher is located at the coordinates of 35°17′ 13.3973″ N, latitude and 4°16′5.81″ E, longitude with an average altitude of 450 m above sea level. Morphologically, the study area is made up of sand dunes and recent alluvial deposits and isolated rocky hills such as mount Meharga, mount Kerdada (Aissaoui 1989). This area is constantly exposed to wind erosion due to the sandy texture and lack of natural vegetation cover (Fig. 1). Topographically, the study area extends from Mount Kerdada, Maalleg and Tsegna to the south, from Mount Mabakhira, Gharhor to the southwest and from Chott Hodna to the north and northeast (Fig. 2).

Climatically, the region has an arid to semi-arid climate, which is influenced by the southern part of the Sahara. Generally, the climate has a cool and humid season in winter and a hot and dry season in summer (Ladgham Chicouche and Zerguine 2001). Low and poorly distributed rainfall throughout the year and variable from year to year (Boudjemline and Semar 2018; Dekkiche 1976), the mean annual rainfall is estimated to be 225 mm and the mean monthly temperature is 21.9 °C. For water resources evaluation in the Maadher region, three wadis are considered i.e., Bousaada, Roumana and Maîter. The first two wadis drain to the depression of the region and the third wadi of Maîter drains to the chott, as shown in Fig. 1. All these wadis contribute to the recharge of the water table. In 1970, the plain of Maadher became a large agricultural perimeter irrigated by the pumping of groundwater.

Climatic, geological and topographical factors greatly influence the presence of groundwater in the Maadher region (ANRH 2006). Similarly, geology and geological structures (faults, fractures and lithological contacts) play a large role in the movement of groundwater in the study area.

Based on different geological studies carried out on the sedimentary successions of the Hodna basin, different cycles of transgression-regression have occurred with marine transgressions ranging from the Early Jurassic or Upper Triassic to the Late Cretaceous (Guiraud 1973; Herkat and Guiraud 2006). The Triassic appears to the south of the mountains of the Hodna basin and the Cretaceous limestone occurs to the south and north of the basin (Fig. 3). Miocene sandstone is transgressed in the Cretaceous. Carbonate deposits fill the southern areas of the mountain range; the Lower Eocene is composed of gypsum marls, phosphate limestone and flint limestone (Askri et al.

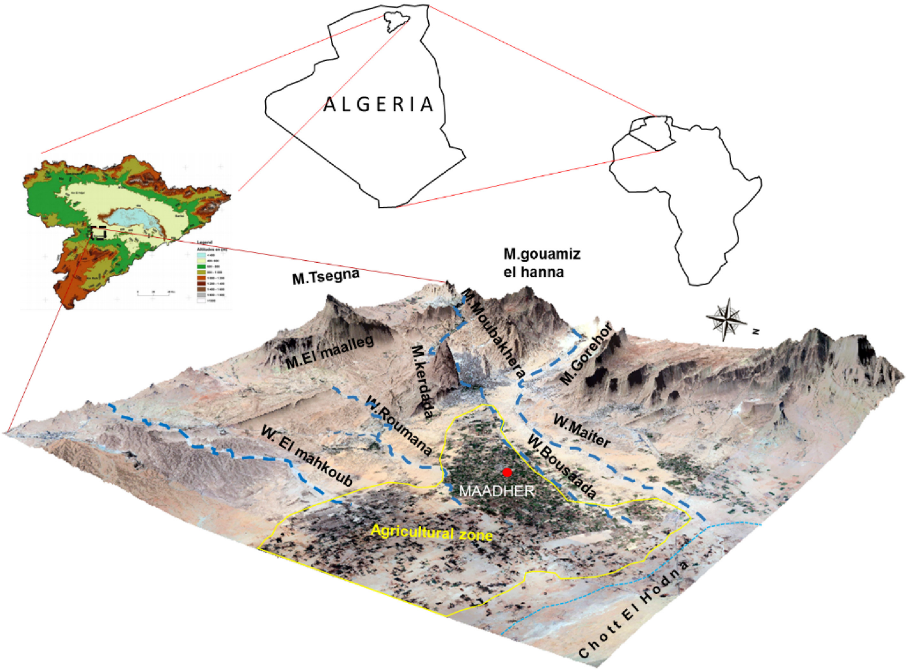


Fig. 1 The geographical position of the study area

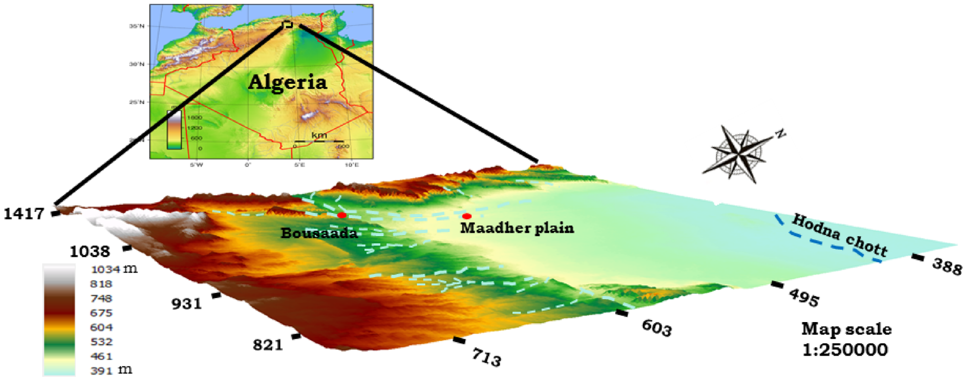


Fig. 2 Topography and drainage map of the Maadher region

1995). The quaternary is accumulated in the center of the basin and rests on a marly substrate.

The geometry of the Mio-Plio-Quaternary aquifer exceeds 250 m in thickness at the center of the plain (Derekov 1973; Guiraud 1973). Thus, the stratigraphy of the study area contains several alternations, often disordered, of clays, sandy clays, sandstone or sometimes clayey sands and conglomerates at the top. The main aquifers in the study area are conglomerates and sandy formations of the continental Mio-Pliocene, which communicate with all the permeable formations of the Cretaceous, of which the most important is the Albian (Guiraud 1970). The latter has a large reservoir that extends to the west, where it outcrops at higher altitudes, where recharge of the aquifer takes place. The Albian contains an aquifer where the water flows in the Tertiary formations, but also in-depth towards the North, to feed the artesian springs which are at the limits of Chott (Derekov 1973). The water table is supplied mainly by infiltration of water wadi and irrigation water. The separation layer between the phreatic aquifer and the deep aquifer is defective and fissured so that the aquifers can communicate with each other (Abdesselam et al. 2013). Since the 1970s, a drop in the groundwater level of more than 15 m has been recorded (ANRH 2006). Groundwater in the quaternary aquifer has a relatively high salinity compared to that in the deep aquifer. The deep aquifer (Pliocene-Miocene) is made up of marls and intercalated conglomerates (continental Tertiary); the interchange between the aquifers is present and the renewable of these aquifers is ensured (Derekov 1973; ANRH 2006).

2.2 Sampling and analysis

The water samples from boreholes in the study area were collected to analyze the major anions and cations. The

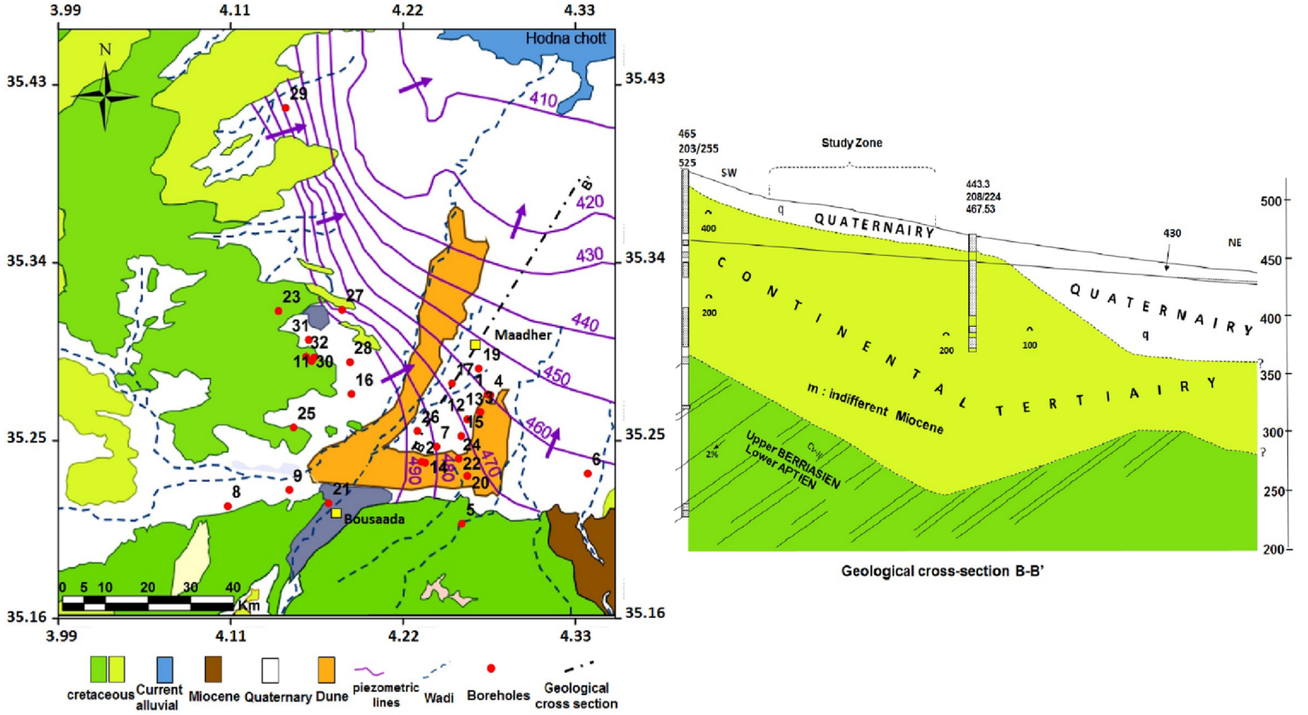


Fig. 3 Geological map with the position of boreholes and hydrogeological cross-section along B-B′ axis

standard method procedure was followed for analysis. Recent samples were taken in clean polyethylene bottles from 32 boreholes after every 10–15 min of pumping; the sampling campaign is made from March to April 2019. The temperature, pH and electrical conductivity (EC) were measured in the field. The samples were collected following the standard methods of sampling protocol (Rodier et al. 2016), were immediately transferred to the Algerian Water Authority Laboratory for analysis. The major ions, Ca^{2+}, Mg^{2+}, HCO_3^- and Cl^- were analyzed by volumetric titration. For Ca the sample is treated with NaOH liquid and Murexide reagent, for TH the sample is treated with NH_4OH and eriochrome reagent. The Mg concentration is the product of the difference between TH and Ca concentration. Cl concentration was evaluated using the Mohr method; the Potassium chromate solution is added to the sample and it is titrated using $AgNO_3$ (0.01 N) solution. To determine the concentration of $HCO^{-}{}_{3}$, the sample is titrated using HCl (0.1 N) solution until the pH of the sample changes to 4.3. The Na^+ and K^+ concentrations were measured using a JENWAY 6850 flame photometer and that of the sulfate by a turbid metric method. The nitrates were analyzed by using visible UV/vis ODYSSEY DR 2500 spectrophotometry. For each analysis of the parameters, the measurement is repeated at least twice. Total dissolved solids (TDS) in water are measured by the weight of deposits left when a water sample has been evaporated to dryness (gravimetric techniques).

The water samples from the boreholes were mainly taken from the Mio-Pio-Quaternary aquifer, where the depths of these boreholes exceed 120 m. Water quality data archive from boreholes for the 1996 and 1967 campaigns are used for comparison. Analyzed water chemistry data were used to determine water quality variables in the study area and to correlate these variables with geology, agricultural inputs and anthropogenic sources. In addition, these variables were used to prepare data input for hydrogeochemical model analyses. The chemical data can be plotted on a Piper diagram (Piper 1944) to interpret the general processes of geochemical evolution of groundwater in the study zone. The Piper diagram is used in the literature to illustrate trends in the chemical evolution of groundwater based on chemical facies.

2.3 Multivariate statistical

The best approach to avoid misinterpretation of quality monitoring data is the application of multivariate statistical methods for the classification and modeling of environmental data (ANRH 2006). Principal component analysis (PCA) and hierarchical cluster analysis (HCA) were applied to a set of groundwater quality data collected in a plain of Maadher using Excel 2010 (Microsoft Office®) and XLSTAT 2016 software. PCA is used in exploratory data analysis of water quality. The aim of the treatment is to identify the principal components that control the chemistry of groundwater (Dougha and Hasbaia 2019; Esmaeili et al. 2018). In addition, HCA has also been used to determine hydrochemical clusters that might be significant in the geological context (Esmaeili et al. 2018).

2.4 Hierarchical cluster analysis (HCA)

This is a multivariate statistical analysis and powerful classification method to divide water chemistry samples into similar groups and useful for data reduction and to check the overlap/continuity of clusters or similarities within the water chemistry data (Esmaeili et al. 2018; Güler and Thyne 2004). Moreover, it is an independent cluster technique and a quantitative method allowing the classification of groundwater into coherent groups that can be identified based on aquifer lithology, storage time, human impact and the correlation with water quality parameters (Rao and Chaudhary 2019). Its objective is to classify samples and variables into few groups based on similarity using the Euclidean distance, and it is grouped according to Ward's aggregation method (Chitrakar et al. 2020; Mir and Gani 2019). Ward's method was more successful to form clusters that are more or less homogeneous and geochemically distinct from other clusters (Cloutier et al. 2008). A study by Sharma (1996) suggests that Ward's clustering procedure is the best, as it produces a greater proportion of observations classified as correct than most other methods. The application of HCA in Q-mode is to determine the main sources of hydrochemical variation and the main spatial associations of groundwater (Dougha and Hasbaia 2019). Spatial clusters defined by Q-mode analysis help to define the spatial distribution of lithological or hydrochemical conditions that represent the underlying processes (Güler and Thyne 2004). The result is a two-dimensional hierarchical dendrogram that recognizes the geochemical relationships that exist between samples and geochemical provinces (Alther 1979; Chitrakar et al. 2020). A small distance shows that two objects are similar or closer, while a large distance indicates a dissimilarity (Tatou et al. 2017).

2.5 Principal component analysis (PCA)

This analysis is a multivariate statistical method, which is used to reduce the number of variables, without sacrificing too much information (Chitrakar et al. 2020; Bouteraa et al. 2019; Zhang et al. 2018; Granato et al. 2018). The method allows exploring the links between variables and similarities between individuals (Granato et al. 2018); thus it is used to identify important components or factors that could explain the variance of a large amount of data and associated variables, and convert them into small string variables according to the principal components (Tatou et al. 2017).

The aim of PCA is to summarize the correlations among a set of observed variables with a smaller set of linear combinations. So, the first step of the method is doing is creating a correlation matrix of those variables, and basing everything else on it. Pearson's correlation coefficient is a numerical measure of the correlation between two correlated variables or pair of variables (x_i, y_i) and is denoted by R. It measures the strength of the linear relationship between these variables. Let (x_i, y_i), $i = 1, 2...n$ represents n pair of values then the coefficient of correlation between x and y is expressed as:

$$R = \frac{\sum_{i=1}^{n}(x_i - \overline{x})(y_i - \overline{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \overline{x})^2 \sum_{i=1}^{n}(y_i - \overline{y})^2}} \qquad (1)$$

where the value of R lies between − 1 and + 1. However, in the case of R = + 1, − 1 and 0 indicate the perfect positive correlation, perfect negative correlation and no correlation respectively between the pair of variables.

This technique has been extended to groundwater quality monitoring, where it is possible to assemble water samples and establish correlations between physicochemical parameters and water samples (Gangopadhyay et al. 2001; Zakaria et al. 2021).

3 Results and discussion

3.1 Hydrogeochemical parameters of groundwater

Most of the sample analysis results showed comparable constituents and the overall precision of the analysis from the control samples is acceptable. The precision of the analytical ion measurement is given by calculating the absolute ion balance (IB), which in all samples has a charge balance error of less than 6%.

The result in Table 1 shows that the groundwater temperature in the study area varies between 12.5 and 30.5 °C for an average of 20.2 °C. The pH is between 6.6 and 7.91 for an average of 7.36. According to the pH standard, these waters are acceptable. The electrical conductivity (EC) of groundwater varies between 1071.29 and 3582.07 µS/cm for an average of 1957.28 µS/cm. The EC is high overall where the water is mineralized. The calcium (Ca^{2+}) ranges from 88.0 to 544.00 mg/L with an average of 275.50 mg/L in all the samples, which is the most represented cation. It is found to exceed the standard in many boreholes. Magnesium (Mg^{2+}) is represented in these groundwater samples in low to moderate proportions, its content varies from 34.00 to 156.00 mg/L for an average of 98.94 mg/L. Sodium (Na^{+}) varies from 27.00 to 290.00 mg/L, the

Table 1 The statistical description of physicochemical parameters for 32 groundwater samples in the study zone

Parameter	Algerian standard (2011)	WHO Standard (2006[a], 2011)	Min	Max	Average	SD
TDS	–	1000	347.00	1274	787.84	240.42
T	25	–	12.5	30.5	20.2	4.9
pH	6.5–9.0	6.5–8.5	6.6	7.9	7.36	0.26
EC	2800	1500[a]	1071.29	3582.07	1957.28	642.28
Ca^{2+}	200	75[a]	88.00	544.00	275.50	138.36
Mg^{2+}	150	100[a]	34.00	156.00	98.94	38.98
NH_4^+	0.05–0.5	1.5	0.02	0.02	0.02	0
HCO_3^-	–	300	235.00	488.00	346.79	69.12
Cl^-	500	250	67.00	479.00	257.89	137.96
SO_4^{2-}	400	250	250.00	990.00	604.06	165.61
TH	200	500	460.00	1920.00	1085.93	462.34
NO_3^-	50	50	7.00	184.00	74.84	48.87
Na^+	200	60[a]	27.00	290.00	89.47	57.41
K^+	12	20[a]	0.90	11.40	5.52	1.99
NO_2^-	0–0.1	–	0.02	0.02	0.02	0
Po_4^-	0–0.5	–	0.10	0.10	0.1	0

All parameters in mg/L except; Electrical conductivity (EC) at 25 °C in µS/cm; Temperature (T) in °C

TDS, total dissolved solids; TH, total hardness

[a] World Health Organization (WHO) (2006), Algerian standard (JORA 2011)

average value is 89.47 mg/L. Groundwater samples contain small potassium (K^+) values ranging from 0.90 to 11.40 mg/L with an average of 5.52 mg/L. The cation analysis shows that the order of importance is $Ca^{2+} > Mg^{2+} > Na^+ > K^+$.

Sulfate (SO_4^{2-}) is the most abundant of the anions. In the samples analyzed, their content goes from 250.00 to 990.00 mg/L for an average of 604.06 mg/L. The bicarbonate (HCO_3^-) contents vary from 235.00 to 488.00 mg/L with an average of 346.79 mg/L. As for the chlorides (Cl^-), their content is between 67.00 and 479.00 mg/L, with an average of 257.89 mg/L. In a worrying proportion, the nitrate (NO_3^-) contents are between 7.00 and 184.00 mg/L with an average of 74.84 mg/L, it exceeds the norm in most boreholes. Consequently, the average content of anions in water, sulfate largely dominates followed by bicarbonate, chlorides, and finally nitrates, in the order of $SO_4^{2-} > HCO_3^- > Cl^- > NO_3^-$.

In addition, the strong correlation between EC measurements and TDS (measured by the weight of deposits left when a water sample has been evaporated to dryness) indicates that conductivity of the groundwater samples increases due to dissolutions of more dissolved inorganic ions. According to the WHO (2011) standards, out of the 32 samples about 87.5% of them fall within the range of WHO allowable TDS concentration (< 1000 mg/L) and is classified as fresh water. The remaining 12.5% are above the TDS concentration of WHO standards (> 1000 mg/L), which is classified as brackish water type. Most of the samples show fairly high TDS values. The increase in the electrical TDS of the groundwater samples is mainly due to the chemical parameters SO_4^{2-}, Cl^-, NO_3^- and Ca^{2+}.

3.2 Correlation of total dissolved solids and major elements (ions)

The relation between the major ions and TDS is illustrated in Table 2. Similarly, remarkable correlations are observed between TDS and (SO_4^{2-}, Cl^-, NO_3^- and Ca^{2+}). These correlations indicate ionic influences resulting from various geochemical interactions such as oxidation–reduction and ion-exchange processes. Both SO_4^{2-} ($R = 0.78$) and Cl^- ($R = 0.75$) anions are most correlated with TDS, indicating major contributors to groundwater salinity. Sources of sulfate in groundwater include mineral dissolution, atmospheric deposition, and other anthropogenic sources (fertilizers, etc.). Gypsum is a major contributor to high sulfate levels in many aquifers around the world. The presence of chloride in groundwater can result from a number of sources, including soil weathering, salt-bearing geological formations (halite). Moreover, the correlations between NO_3^- and Ca^{2+} concentrations against TDS are rather moderate ($R = 0.62$ and $R = 0.54$, respectively). The presence of nitrate highlights the predominance of anthropogenic activities. The moderate correlation of calcium justifies the occurrence of ion exchange, increasing

Table 2 Correlation matrix of the physicochemical parameters of the groundwater samples

Parameter	TDS	T	pH	EC	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	Na^+	K^+
TDS	**1**											
T	− 0.188	**1**										
pH	− 0.346	0.283	**1**									
EC	**0.941**	0.135	− 0.281	**1**								
Ca^{2+}	**0.539**	− 0.072	− 0.152	**0.519**	**1**							
Mg^{2+}	0.248	− 0.245	− 0.072	0.183	**0.551**	**1**						
HCO_3^-	0.235	− 0.013	0.227	0.211	0.369	0.319	**1**					
Cl^-	**0.751**	− 0.167	− 0.256	**0.671**	**0.776**	0.398	0.398	**1**				
SO_4^{2-}	**0.781**	− 0.105	− 0.272	**0.757**	**0.788**	0.453	0.240	**0.694**	**1**			
NO_3^-	**0.623**	− 0.263	− 0.267	**0.542**	**0.554**	0.412	0.048	**0.526**	**0.524**	**1**		
Na^+	0.300	− 0.193	− 0.073	0.218	**− 0.47**	**− 0.607**	− 0.043	− 0.038	− 0.093	− 0.21	**1**	
K^+	0.324	− 0.109	− 0.058	0.263	− 0.38	**− 0.464**	− 0.107	0.043	− 0.030	− 0.26	**0.831**	**1**

All parameters in mg/L except; Electrical conductivity (EC) at 25 °C in µS/cm; Temperature (T) in °C

The bold value shows the strong correlation and inverse correlation between the Physico-chemical parameters

the concentration of sodium in the water to the detriment of calcium.

The weak correlation between HCO_3^- concentrations and TDS is mainly due to calcite precipitation in the water (The increase in water temperature of an aquifer system decreases the amount of carbon dioxide (CO_2) dissolved in the water and causes the precipitation of calcite [$Ca(HCO_3)_2$] which reduces the HCO_3^- concentrations (Mitchell et al. 2019). The remaining ions having a low correlation coefficient with TDS (Table 2), showing proportionally less contribution to groundwater salinity. In general, the main factors controlling the chemical composition of groundwater in the region include evaporation, dissolution, ion exchange and precipitation. In addition, the contributions of human activities are superimposed in certain regions, in particular areas with intensive human activities.

3.3 Hydrogeochemical water classification using piper diagram and multivariate methods

The Piper diagram has been widely used to show water classifications and water quality trends for groups of samples (Dalton and Upchurch 1978). The major ionic species present in most natural waters are Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, HCO_3^- and SO_4^{2-} (Fetter 2018). The term hydrochemical facies is used to describe bodies of groundwater in an aquifer, which differ in their chemical composition (Fetter 2018).

Overall, the Fig. 4 shows that the groundwater in the study area has a dominant hydrochemical facies of sulfate–chloride–nitrate–calcium (SO_4^{2-}–Cl^-–NO_3^-–Ca^{2+} type water). Out of 32 samples, 84.37% of the samples belong to the SO_4^{2-}–Cl^-–NO_3^-–Ca^{2+} type, 12.5% of the samples belong to the Ca^{2+}–Mg^{2+} type and only 3.1% of the samples belong to the SO_4^{2-}–Cl^-–NO_3^- type. With nearly 16 samples rich in calcium, 01 sample number 29 rich in sodium and potassium, 01 sample number 18 rich in chloride and almost 15 samples without a dominant chemical element (between Ca^{2+}–Mg^{2+}–Na^+). These water types illustrate the presence of permanent hardness in the groundwater of the study zone. Thus, it can be suggested that hydro-geochemistry be controlled by the three general processes that contribute to solute control in groundwater: evaporite dissolution, carbonate dissolution, and silicate weathering (Deutsch 2020). The evolution of water chemistry depends not only on the overall chemistry of the water/rock interaction, but also on the rate of weathering, Li et al. (2018) showed that the weathering rates of evaporites and carbonates are faster than silicate weathering rates.

Accordingly, the evolution or spatial variability of the composition of the few major ions in groundwater can be used to trace the type of aquifer and the hydrogeochemical processes taking place in the study area (Güler et al. 2002). While the mixed zone of the piper diagram (84.37% of the samples) belongs to the category of permanent hardness giving an indication of groundwater originating from carbonate formations (limestone and dolomite) and evaporite deposits (gypsum) or from zones of active recharge with short residence times (Hounslow 1995) and also with the presence of anthropogenic pollution.

Also, according to the average values in Table 1 which indicate the dominance of alkaline earths over alkalis (i.e., $Ca^{2+} + Mg^{2+} > Na^+ + K^+$), and strong acid anions exceed weak acid anions (i.e., $SO_4^{2-} + Cl^- > HCO_3^-$).

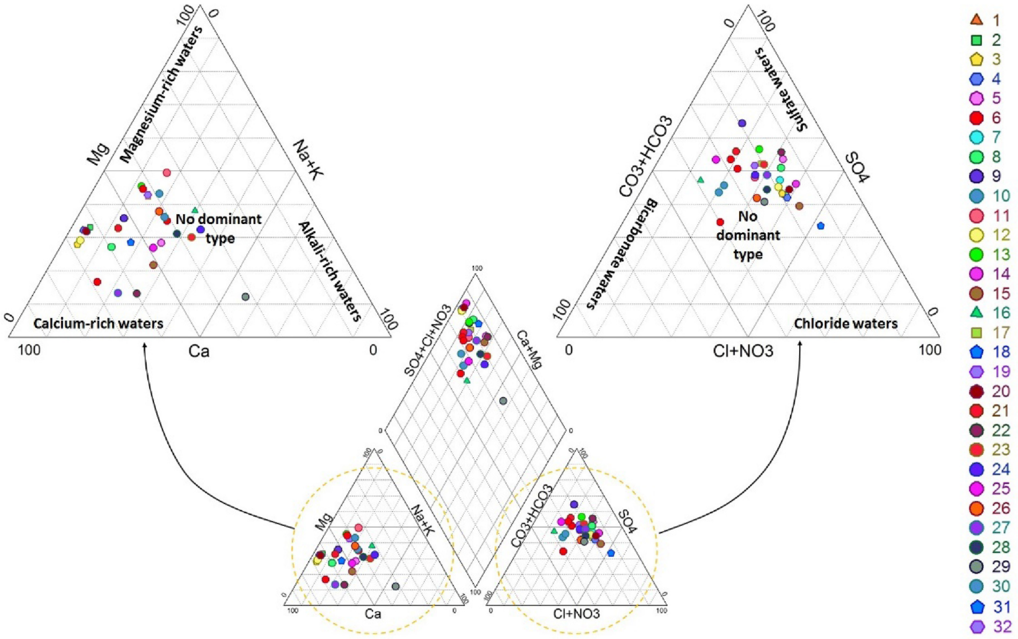


Fig. 4 The Piper diagram illustrates the classification of groundwater

3.4 HCA and PCA analysis

Accordingly, HCA and PCA classifications are carried out after the preparation of the hydrochemical data table according to the Xlstat software model. Altogether 13 parameters taken into account, including TDS and EC, were used in the calculation of the multivariate analysis which will have the effect of giving more weight (variability) to water salinity.

HCA classification was conducted after all hydrochemical data were log-transformed and standardized to have equal weights. Use Standard Scaler from Scikit Learn to standardize the dataset features onto unit scale (mean = 0 and standard deviation = 1) as described by Güler et al. (2002). The classification was done based on the dissimilarity and Euclidean geometric distance between observations. The advantage of the HCA method is that it does not require any prior knowledge of the number of clusters (Rahbar et al. 2020). Here, HCA was applied using dissimilarity which can be defined as the distance between two samples according to a criterion (how different are these samples?). As there is no test to determine the optimal number of clusters in the data set (Güler et al. 2002), visual inspection is the only criterion for selecting clusters in the dendrogram (Fig. 5). The defined phenon line (Sneath 1973) was chosen at a dissimilarity distance of 2.5 E + 06. At this distance, groups can be distinguished based on their hydrochemical variables. The result proven by the hierarchical cluster analysis on the set of 32 samples is shown in Fig. 5; the dendrogram shows three groups with distinct characteristics. In addition, the elemental compositions of the water samples by cluster have been averaged and summarized in Table 3.

Cluster C1 contains 11 samples (1, 2, 3, 4, 7, 12, 14, 15, 20, 22 and 24) that have relatively high mineralization (the average TDS is 1011.45 mg/L), the dominant parameters of this group are TDS, EC, Ca^{2+}, Mg^{2+}, Cl^{-}, SO_4^{2-}, NO_3^{-} and HCO_3^{-} (Table 3). Cluster C2 consists of 14 samples (5, 8, 9, 11, 13, 17, 18, 19, 21, 23, 26, 27, 28 and 29) with 43.75% of the total samples. The average TDS is 784.42 mg/L. This group has a high level of Na^{+} and K^{+}. Cluster C3 is represented by 07 samples (6, 10, 16, 25, 30, 31 and 32), and have relatively light mineralization (the average TDS is 443.28 mg/L. This group mainly includes pH and with a relatively high mean value, Fig. 5.

Through these results, the spatial distribution of the clusters is presented in Fig. 6. Each cluster is represented by a colored area whose space is directly proportional to the number and position of the boreholes concerned. Boreholes 29, 23, 11 and 6 are considered isolated in relation to their main zones, i.e., the borehole is far from the center of gravity of its zone or the borehole is on the other side of its zone in relation to the recharge wadis (Bousaada and Maître). This figure made it possible to situate the information and to understand the physico-chemical behavior of the aquifer, the hydro-geochemical evolution along the flow paths (wadi), to separate the zones of recharge and evacuation of the waters and perform inverse geochemical modeling in the future. In general, these quality groups are distinguished by the presence of

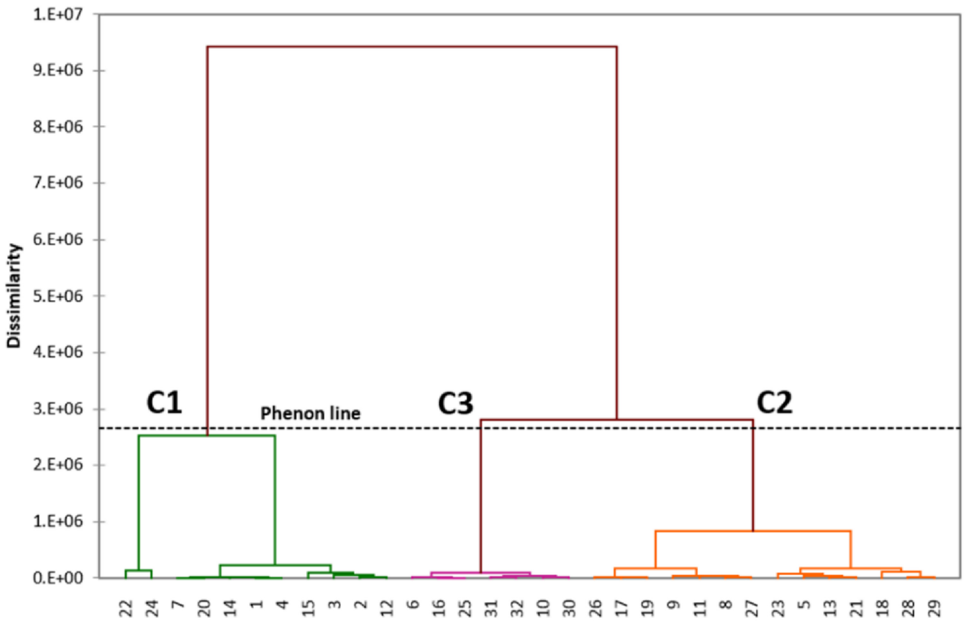


Fig. 5 Dendrogram for the hierarchical cluster analysis showing the three identified clusters

Table 3 Mean physicochemical parameter values for the mean clusters determined by HCA

Cluster	TDS	pH	EC	Ca^{2+}	Mg^{2+}	NH_4^+	HCO_3^-	Cl^-	SO_4^{-2}	NO_3^-	Na+	K+	%Boreholes
C1 (n = 11)	**1011.45**	7.36	**2620.26**	**426**	**122.45**	0.02	**388.18**	**399.45**	**765.45**	**108.54**	72	5.02	34.37
C2 (n = 14)	**784.42**	7.27	1827.63	214.42	93.01	0.02	314.3	222.17	585	75.17	**109.5**	**6.32**	43.7
C3 (n = 07)	**443.28**	7.53	1174.74	161.14	73.85	0.02	346.71	106.85	388.57	21.18	76.85	4.68	21.87

Except pH, EC (µS/cm), and all others in mg/L; n is the number of boreholes by cluster

The bold value shows the high average values of Physico-chemical parameters determined by the HCA method

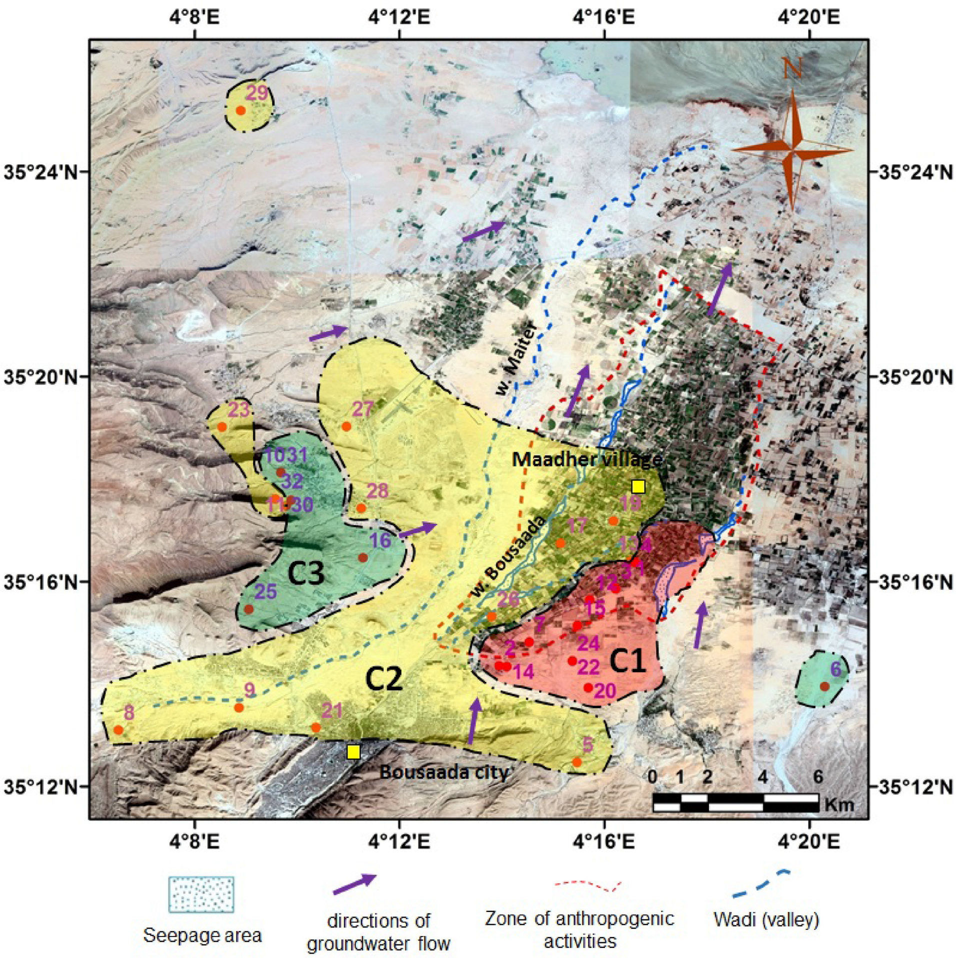
processes: degree of rock-water interactions, residence times of the groundwater in the multilayered aquifer and type of recharge (Yenehun et al. 2021).

Sampling records from the same region are generally assigned to the same cluster during HCA. Cluster C1 is dominated by a SO_4^{2-} –Cl^-–NO_3^-–Ca^{2+} type, Cluster 2 contains has a SO_4^{2-} –Cl^-–NO_3^-–Mg^{2+} type, except the borehole number 29 has Cl^-–Na^+–K^+ type. Groundwater samples in Cluster 3 have a Cl^-–SO_4^{2-}–Ca^{2+}–Mg^{2+} type. Cluster C2 samples are located mainly in the wadi valleys of Maîter and Bousaada. Cluster C1 includes samples that are located in the region near Roumana wadi (source of recharge).

The PCA on the sample data showed that the first three principal components cumulated a percentage of the variance of 74.22%, so it is satisfactory to define the structure of the point clouds. This method makes it possible to reduce the physicochemical parameters by correlation (Dougha and Hasbaia 2019). The Kaiser criterion (Kaiser 1960) was applied to determine the total number of significant principal components. According to this criterion, only the principal components whose eigenvalue is greater than or equal to 1 have been retained as a possible source of variance in the data. Table 4 shows the variance expressed by each principal component and shows its importance relative to the other principal components. The principal component PC1 represents 40.45% of the variance of physicochemical parameters (Table 4) and is attributed to a strong correlation with the following parameters EC, Ca^{2+}, Cl^-, SO_4^{2-}, Mg^{2+} and NO_3^- (Table 4 and Fig. 7). The principal component PC2 (22.16%) combines Na+ and K+. Principal component PC3 takes 11.61% of the variance of water quality and shows a good correlation with bicarbonate (Fig. 7).

Application of HCA and PCA methods to water samples could divide the waters of the area into three groups; each group contains the most correlated and similar elements in the water samples. Based on the score graph, we can conclude that clusters C1, C2, and C3 are driven by PC1. The cluster C3 is the low negative side of PC1 and the cluster C1 is the high positive side, where high values for EC, Ca^{2+}, Cl^-, SO_4^{2-}, Mg^{2+} and NO_3^- yield a strong positive value of PC1. In addition, cluster C2 is characterized by intermediate PC1 values and PC2 values, which are driven by high PC2 values (Na^+, K^+). PC1 explains the largest part of the variance in the data (40.45%) indicating

Fig. 6 Schematic presentation of clusters by HCA in the study zone (for drinking water)



mineralization. Although the HCA dendrogram suggests that the clusters C2 and C3 could be merged if a higher threshold (phenol line) was selected. The clusters are separated mainly by their PC1 score (mineralization). This observation allows a better interpretation of the results and the underlying structure of the clusters (Fig. 8).

4 Discussion

4.1 Impact of overexploitation of aquifer on quality water

Assessing the quality of water for domestic use is very important due to its direct impact on human welfare. Figures 9 and 10 illustrate the evolution of the major ions and in particular the EC and the sulfate following different measurement campaigns of water quality in 1967, 1996, and 2019. According to the sampling campaigns, the relative decrease in EC and sulfate values is explained by the order of exploitation of the quaternary aquifer (more salty mineral water) than the deep aquifer (relatively less salty mineral water); Due to the lowering of the water level of the shallow aquifer, the exploitation of the deep aquifer started in the 1990s. Figure 10b shows that since the 1970s, nitrate concentrations have been high in most boreholes in the study area. A significant number of water samples for nitrate ion exceeds the WHO standard (50 mg/L). The diffusion of the nitrate element in the Pio-Mio-Quaternary aquifer is observed in the measurement campaign the 2019, the majority of the boreholes are affected by an increase in concentration. This could be due to soil leaching and anthropogenic effects, such as mixing of chemicals and animal wastes during irrigation, traces of waste water with wadi water resources. Nitrate concentration above the norms found in the agricultural part of the study area.

4.2 Origin of the major ions parameters in groundwater

The concentrations of major ions are controlled by complex interactions between many factors and various mechanisms. The moving water through the sedimentary formations (alluvium, sand, gravel, evaporator, deposit,

Table 4 Principal components, eigenvalues and total variance for the groundwater quality parameters

	TDS	T	pH	EC	Ca^{2+}	Mg^{2+}	NH_4^+	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	Na^+	K^+	Eigenvalue	Variability %	Cumulative %
PC1	**0.861**	− 0.193	− 0.339	**0.803**	**0.855**	**0.576**	0.00	0.366	**0.868**	**0.888**	**0.734**	− 0.164	− 0.11	4.854	**40.453**	40.453
PC2	0.473	− 0.128	− 0.24	0.418	− 0.337	− 0.572	0.00	− 0.148	0.102	0.066	− 0.097	**0.935**	**0.908**	2.659	**22.16**	62.613
PC3	0.034	**0.652**	**0.662**	0.22	0.103	− 0.12	0.00	**0.58**	0.114	0.062	− 0.3	0.054	0.101	1.394	**11.613**	**74.226**

The bold value shows the strong correlation between Physico-chemical parameters and principal components

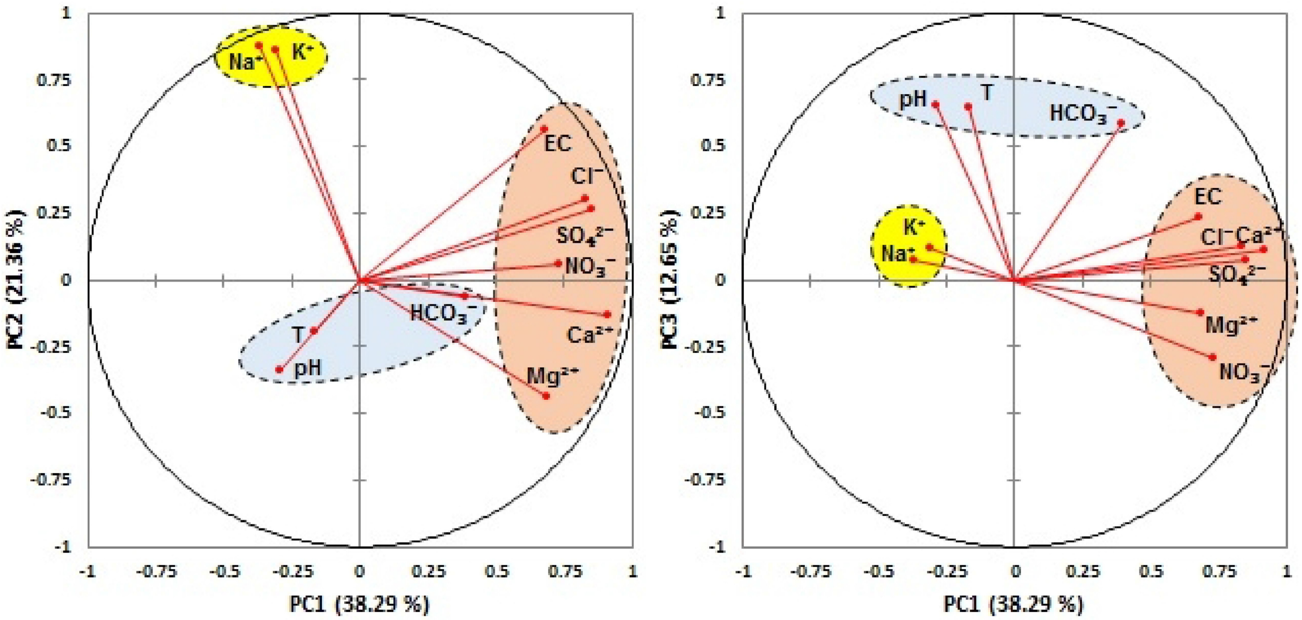


Fig. 7 Correlation between the principal components using PCA method

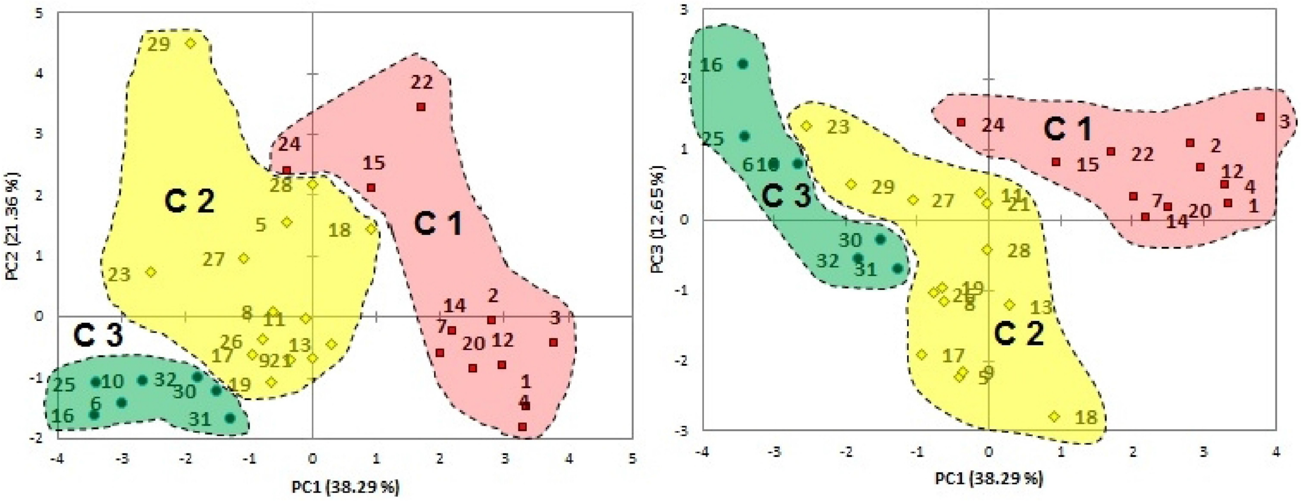


Fig. 8 Overview of clusters on Score Plots PC for PC1 vs. PC2 and PC3

etc.) of the mixed (quaternary/deep) aquifer along circulation paths control the chemical process of the water. The Fig. 11 shows the significant effect of calcium versus magnesium ions on EC as well as for sulfate versus chloride ions. In addition, the predominance ions of Cl^- over Na^+ on the EC are also shown. The presence of Cl^- in the Maadher aquifer may result from a number of sources, including saliferous [halite (NaCl)] geological formations (Khelif and Boudoukha 2018), as well as partly through soil weathering (Panno et al. 2006), i.e., the recharge of the Maadher aquifer comes from the infiltration of the Bousaâda wadi floods in their alluvial depression zones which are located in the study area. Additionally, Fig. 11b indicates that the molar ratio Cl^-/Na^+ is more important in the samples of cluster C1 than C2 and C3.

In Fig. 11a, most water sample points are plotted above the equal ratio 1, the SO_4^{2-} versus Cl^- plot implies a low chloride concentration. Sulfate content in groundwater can be attributed to the dissolving gypsum ($CaSO_4$–$2H_2O$) in water. In addition, if the molar ratio Ca^{2+}/Mg^{2+} = 1, dissolution of dolomite [CaMg $(CO_3)_2$] should occur, whereas a higher ratio is indicative of greater calcite contribution (Li et al. 2018). The molar ratio of $Ca^{2+}/Mg^{2+} > 2$ indicates the dissolution of silicate minerals, which contribute

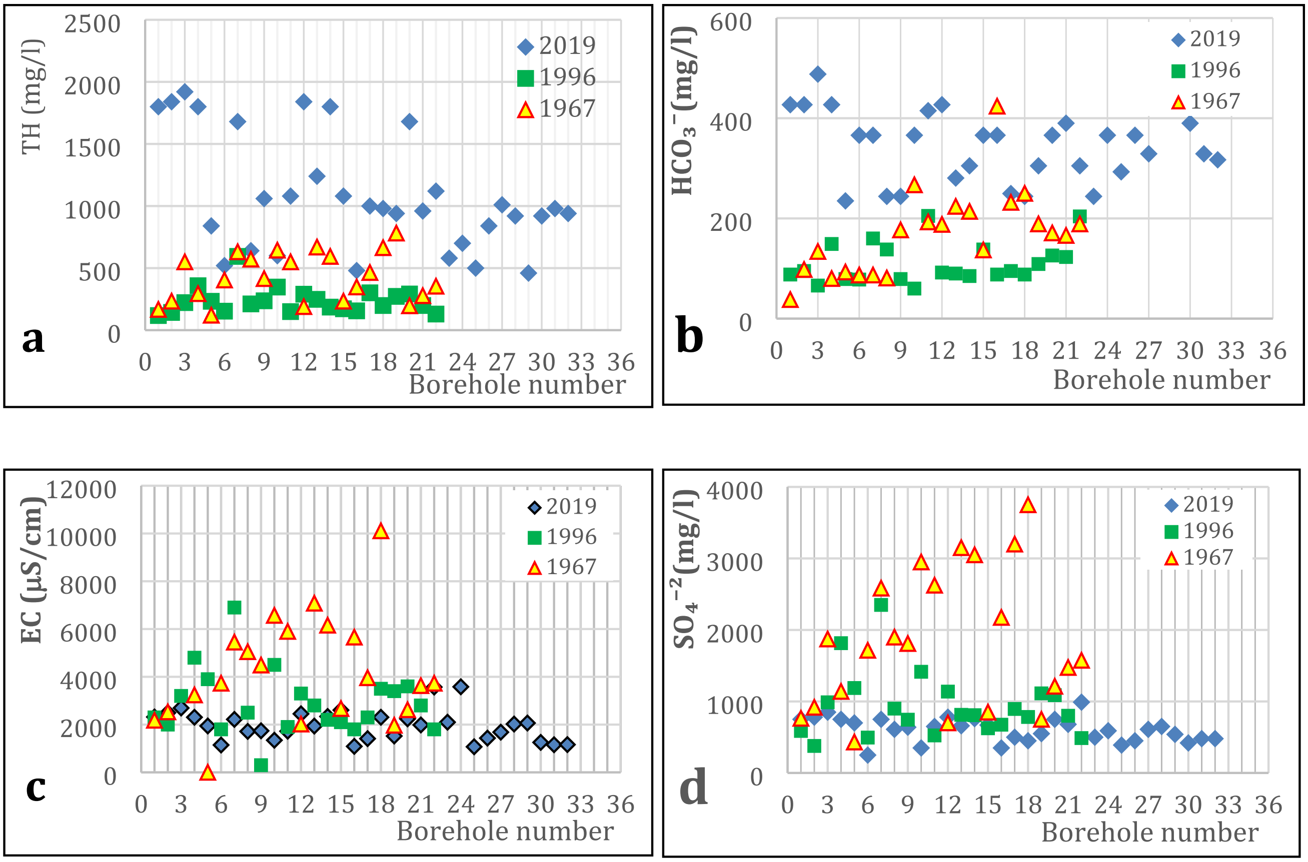


Fig. 9 Temporal evolution of TH, HCO_3^-, EC and SO_4^{2-} in the Maadher area following different measurement campaigns

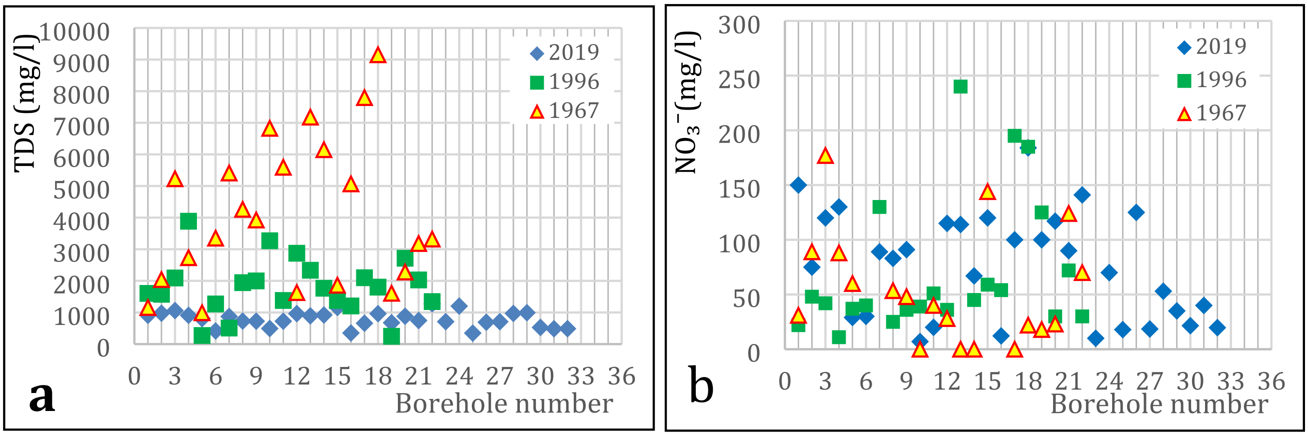


Fig. 10 Temporal evolution of TDS and NO_3^- in the Maadher area following different measurement campaigns

calcium and magnesium to groundwater (Kshetrimayum and Laishram 2020). Figure 11d shows that most of the water samples of cluster C1 have a ratio greater than 2, which probably indicates the influence of clay minerals (inverse cation exchange) and/or gypsum dissolution. All the water samples of cluster C3 are characterized by the dissolution of dolomite.

The reaction of carbonate minerals (calcite and dolomite) with water and carbon dioxide is written as follows:

$$\underbrace{CaCo_3}_{Calcite} + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \tag{2}$$

$$\underbrace{(CaMg(CO_3)2)}_{dolomite} + 2H_2CO_3 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \tag{3}$$

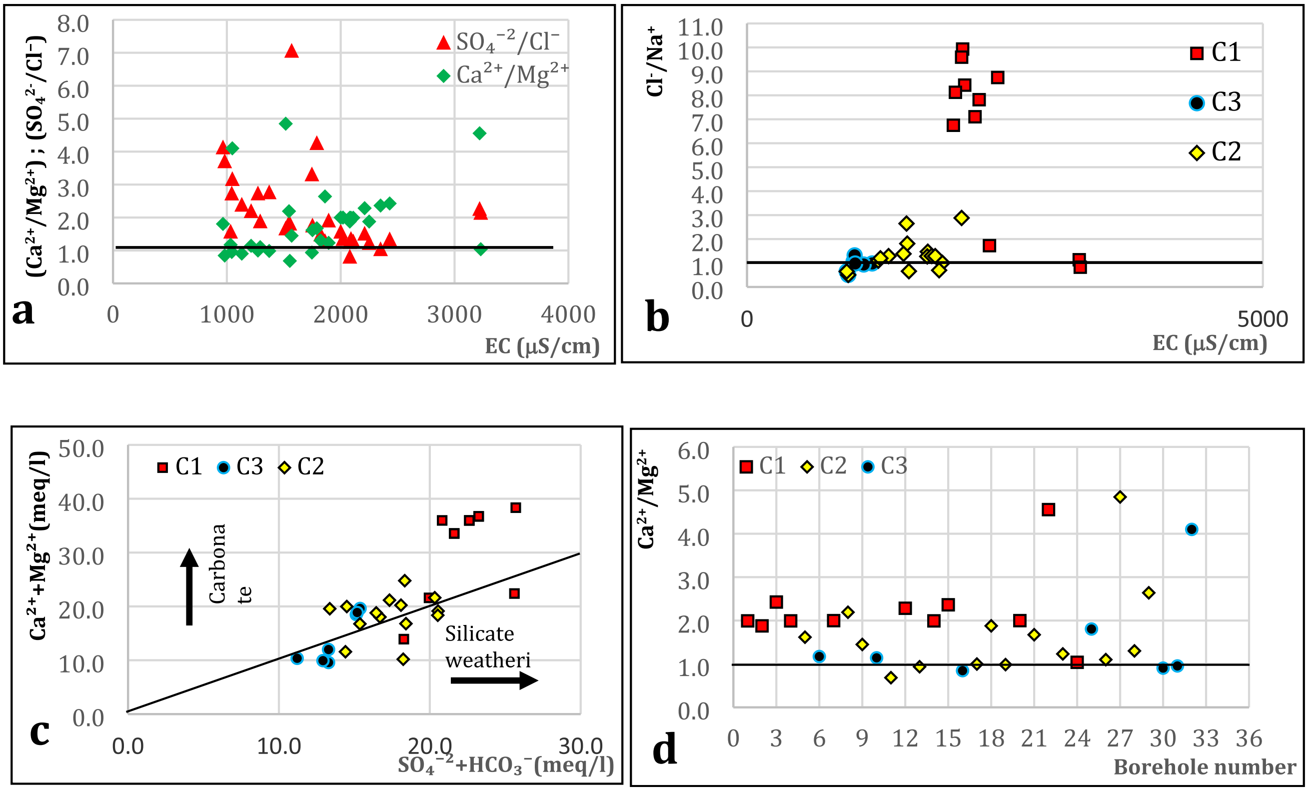


Fig. 11 Bivariate plots of **a** EC against (Ca^{2+}/Mg^{2+}) and (SO_4^{2-}/Cl^-). **b** EC against (Cl^-/ Na^+) vs. (Under Na^+ exchange reactions with Ca^{2+} and Mg^{2+} in clay layers). **c** ($SO_4^{2-} + HCO_3^-$) against ($Ca^{2+} + Mg^{2+}$)

The presence of the evaporated sequence (gypsum) in water allows dissolution according to the reaction:

$$CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \quad (4)$$

Most of the groundwater samples found to be below 1 ratio indicates the calcite weathering prominent process. The presence of carbonates and silicates in the sand deposits could favor the weathering process. When ion exchange is an important geochemical process for controlling groundwater composition, the relationship between the diagram ($Ca^{2+} + Mg^{2+}$) and ($SO_4^{2-} + HCO_3^-$) illustrating ion exchange should be linear with a slope of 1.0 (Fisher and Mullican 1997). In Fig. 11c, the plot of ($Ca^{2+} + Mg^{2+}$) versus ($SO_4^{2-} + HCO_3^-$) shows that more than half of the groundwater samples fall to the left of the 1:1 line, which indicates that the reverse ion exchange tends to be dominant over the ion exchange process in the study area. The samples of cluster C1 underwent the process of carbonate dissolution more than the others. The various ionic relationships confirmed the reverse ion exchange process where the Ca^{2+} and Mg^{2+} in the aquifer matrix have been replaced by Na^+ at favorable exchange sites. This phenomenon has accounted for the dominance of Ca^{2+} and Mg^{2+} ions over Na^+ ion at all the sites (Belkhiri et al. 2012). Clay minerals are layered with boundaries and face negatively charged, on which cations can bind and exchange as follows:

$$Ca(Mg) - Clay_2 + 2Na^+ \rightarrow Ca^{2+} + Mg^{2+} + Na + Clay_2 \quad (5)$$

However, when Cl^- concentration increases relative to Na^+, it implies Cl^- released during carbonate weathering (Deutsch 2020). During this process, the aquifer can dissolve sodium in exchange for the bound ions of Ca^{2+} and Mg^{2+}. Also, the sources of Ca^{2+} and Mg^{2+} in groundwater can be deduced from the ratio ($Ca^{2+} + Mg^{2+}$)/HCO_3^-. As this ratio increases with salinity (Fig. 12b), Mg^{2+} and Ca^{2+} are added to the solution at a rate higher than HCO_3^-. Figure 11a, b confirm the salinity growth of the three clusters in the order C3, C2 and C1. The Fig. 13a shows the evolution of the anions as a function of the EC; this figure shows that EC does not change with bicarbonate, while sulfate and chloride ions increase with salinity. High sulfate levels suggest that groundwater be exposed to gypsum and saline elements (Epsom salt, Glauber's salt, fertilizer, etc.) (Medjani et al. 2021). The Fig. 13b the ratio of ions [HCO_3^-/($SO_4^{2-} + Cl^-$)] as a function of EC does not show the clear presence of the two poles (very few trends around the second): the first is a carbonate characterized by a predominantly HCO_3^- ion and the second is gypsum

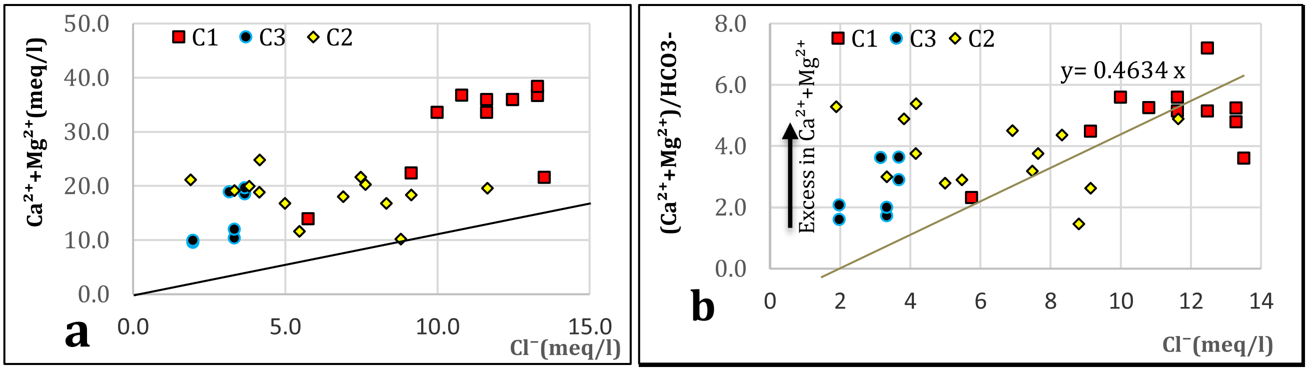


Fig. 12 Bivariate plots of **a** Cl^- against ($Ca^{2+} + Mg^{2+}$). **b** Cl^- against ($Ca^{2+} + Mg^{2+}$)/HCO_3^-

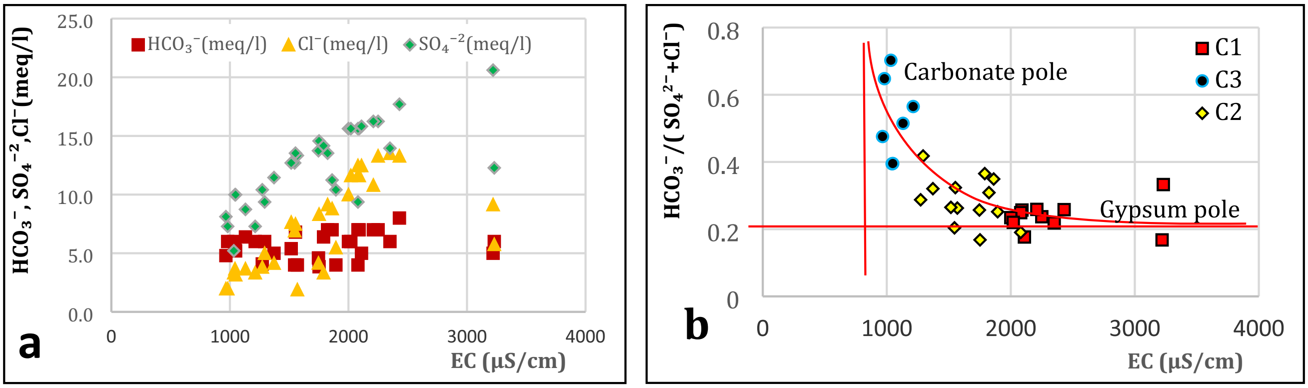


Fig. 13 Bivariate plots of **a** EC against anions. **b** EC against (HCO_3^-/(SO_4^{2-} + Cl^-))

characterized by the dominance of SO_4^{2-} and Cl^- ions. The samples of cluster C3 have a clear tendency toward the carbonate pole, on the other hand, those of clusters C1 and C2 does not have this tendency.

5 Conclusion

The demand for water for domestic and irrigation purposes is growing very rapidly depending on the increase in population and the effect of climate change affecting the countries of North Africa and hence causing over-pumping of water resources in the study area. Limestone, dolomite and gypsum are the main rocks explaining the ionic composition of groundwater in the study area. It is mainly due to carbonate weathering and dissolution of gypsum evaporites. Anthropogenic processes also play an important role in the study area. The recharge of the phreatic aquifer takes place primarily by the flood waters of Bousaâda Wadi which crosses the city upstream and the agricultural practices contribute to the deterioration of the quality. As a result, water quality issues like groundwater salinity are a major concern for water resources development projects as well as human health (drinking water supply). Hydrogeochemical processes and multivariate methods are used as a methodological approach in the assessment.

The results revealed that the groundwater in the Maadher study area as a whole is moderate quality fresh water, due to its total dissolved solids content and other dissolved chemical ions of health concern (Nitrate (NO_3^-) which exceeds the WHO standard in the majority of the samples). The study indicates that the hydrochemical facies of sulfate–chloride–nitrate–calcium (SO_4^{2-}–Cl^-–NO_3^-–Ca^{2+} type), which globally characterizes the study area and these elements are the dominant dissolved ions, where the matrix Correlation analysis has shown that they correlate well with Total Dissolved Solids (TDS) and are also major contributors to groundwater salinity. No typical seawater mixing or base ion exchange was observed in the study area as none of the samples belong to Na^+– Cl^- and Na^+–HCO_3^- types. The contribution of reverse ion exchange processes, the dominance of alkaline earth metals (Ca^{2+}, Mg^{2+}) over alkalis (Na^+, K^+) and strong acid anions (SO_4^{2-}, Cl^-) over weak acid anions (CO_3^{2-}, HCO_3^-) were raised in the study zone. Principle Component Analysis (PCA) and Hierarchical Component Analysis (HCA) methodologies are used to identify if there were different groupings and associations between the borehole waters. Three distinct water groups were found illustrating a different evolution of salinity (EC and TDS). As a first step, the use of HCA grouping method allowed us to separate the mineral and less mineral water from the borehole waters, with significantly higher sulfate, chloride, and nitrate concentrations. The hydrogeological conceptual framework and the GIS map presented in this study make it possible to visualize certain theoretical links between the geology, and the type of underground hydraulic circulation in the aquifer. This is an interesting finding for environmental monitoring, as a well-conducted HCA can identify the contaminated area. Principal component analysis (PCA) is a widely used statistical technique for unsupervised dimension reduction. Q-means clustering is a clustering of observations used to perform unsupervised learning tasks. Overall groundwater quality is average and suitable for domestic purposes and permitted for irrigation use.

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Data availability The data that support the findings of this study are available from the corresponding author, upon a reasonable request.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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