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Research paper

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Monitoring of hydrogeochemistry and hydrological isotopes in karst springs of Tezbent Plateau, Tebessa region, north-east of Algeria

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Summary

The karst springs of Tezbent Plateau were studied to gain insight into the hydrogeological and hydrodynamic behaviour of this karstic system. Four springs and six domestic wells were analysed for hydrogeochemical constituents, δ18O, and δ2H from September 2021 to June 2022. The Tezbent mountain range, located in northeastern Algeria, drains carbonate aquifers through several significant karst springs.

The physical and chemical characteristics of water samples were analysed in order to assess the groundwater origins and identify the factors influencing its geochemical composition. Ionic speciation and mineral dissolution/precipitation were calculated. It was found that geology, specifically the presence of carbonate formations, elevation, and the rate of karst development, are the primary factors influencing groundwater composition and seasonal variations.

The carbonate chemistry serves as a diagnostic indicator of karst development effects. The interaction between groundwater and surrounding host rocks is believed to be the primary process influencing the observed chemical characteristics of groundwater in the study area. The δ18O and δ2H values of groundwater samples indicate the meteoric origin of the groundwater recharge and suggest a minimal evaporation impact on the isotopic composition.

Keywords

karst aquifer • hydrochemistry • isotopes • Tezbent • Algeria

1. Introduction

Groundwater has emerged as the major, or the only, source of fresh water for domestic use in many arid and semi-arid parts of the world, which is a result of decreasing rainfall patterns, reduced availability of surface water and socioeconomic activities. This is also the case of Tezbent mountainous region, where springs are major lifelines and precious resources that play important roles in securing the needs of the people, maintaining balance in the ecosystem and providing riverine base flows. Because of the lack of permanent surface water reservoirs owing to the severe climate conditions, groundwater provides the most available source of fresh water. In this region, groundwater is used for domestic and agricultural purposes [Rouabhia et al. 2009].

A major concern in groundwater research is water quality. Measurements of temperature, pH, electrical conductivity (EC), total dissolved solids (TDS), and major cations and major anions are all part of the hydrogeochemical study of groundwater. These are essential tools and elements that determine the evaluation of water quality. Geological processes and human activity are the sources of groundwater chemistry [Hamad et al. 2021]. Groundwater chemistry and hydrogeological regime studies indicate potential human and geological impact on water quality [Mouici et al. 2017]. They also help water resource management by determining the quality of the water and whether it is suitable for a given use.

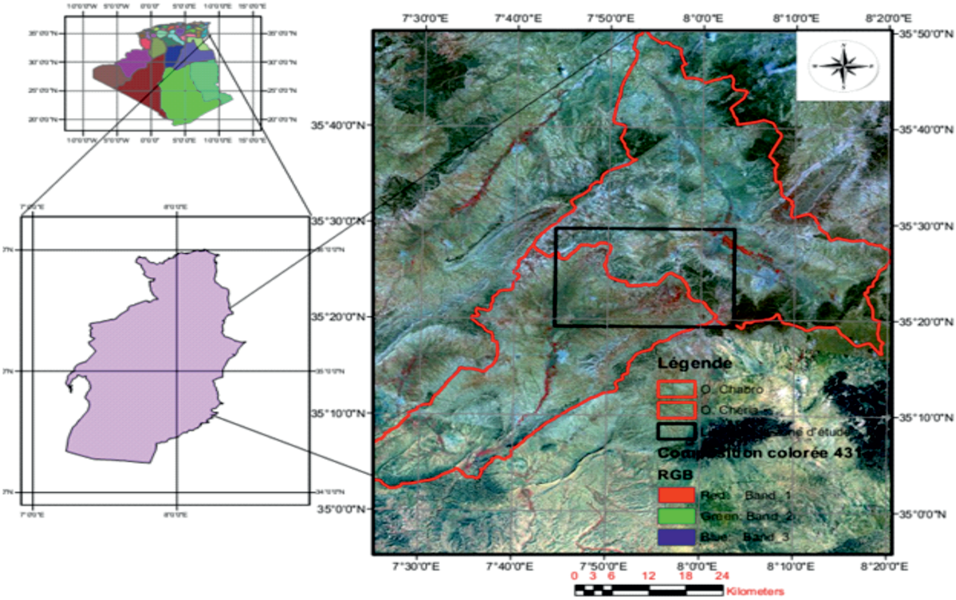

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Fig. 1. Location map of the study area

This study aimed to determine the groundwater chemistry control mechanism, assess the hydrogeochemical properties of the groundwater in relation to water type, and look into seasonal variations in the in-situ physicochemical parameters of the groundwater. The water's fitness for human consumption was also assessed, which required the identification of chemical processes that are responsible for the groundwater chemistry and the reconstruction of the origin and recharge mechanisms of groundwaters.

The studied area is located within the arid zones of Algeria, situated 20 kilometres far from Tebessa city, and is characterised by a precipitation of less than 300 mm per year. It covers about 160 km² (Fig. 1).

2. Study area

2.1. Geography and geology

The research site is a section of a large mountain within the extensive plio-quaternary tectonic plateau of Cherea, situated between 7°45'–8°05' E and 35°15'–35°30' N. The area is bordered by Djebel Doukkane to the East and Djebel Gueriguer to the West, Djebel Gagaa to the North, and it is limited by an administrative boundary to the South (Fig. 1). A semi-arid area with annual precipitation ranging from 250 to 300 mm can indeed be challenging, especially with temperatures reaching up to 40°C in the summer. The declining renewal of water resources over the past decade adds another layer of concern. These factors can have a significant impact on groundwater quality. The combination of dry climate, atmospheric dust, and low precipitation intensity often contributes to water chemistry degradation [Bedini 2009].

The formation of aquifers, and the subsequent recharge and transport of groundwater are both influenced by geology. Due to the interactions between rock and water, these processes are also significant for the quality of the local groundwater. Since groundwater quality is dependent on the total amount and type of minerals dissolved from the surrounding rocks, reactions between groundwater and aquifer materials modify the quality of the water, which is also important for understanding the creation of groundwater. The flow patterns of groundwater and the interactions between water and rock determine the concentration of dissolved ions [Nekkoub et al 2020]. While the anions in groundwater may come from non-lithologic sources, the majority of the cations in the water are obtained from the mineral solutions formed during chemical weathering.

The Hammamet area is a subsidence basin that formed during the end of Luthitien and belongs to the larger Mio-Plio-Quaternary tectonic depression of Tebessa-Morsott. The basin, entirely filled with alluvial sediments, has bedrocks comprising Cenomanian age interspersed marls [Nouioua et al. 2015]. The core of the region is comprised of Pliocene and Quaternary alluvial deposits, predominantly conglomerates, gravels, and sandstones. This aquifer covers the majority of the tectonic depression and is bounded by two faults oriented in a W-E direction (Fig. 2).

The aquifer, with a water table at a depth of 20–30 m, serves both drinking and irrigation purposes. Water level fluctuations between the dry and wet seasons are relatively stable, not exceeding 1.5 m on average. Groundwater typically flows from the southwest to the northeast, and in the sandy sections the average permeability is around 10^{-3} m/day [Djabri 1987]. Precipitation at Djbel Troubia and Djbel Essenn primarily recharges the aquifer, with some influence from wadi recharge or drainage depending on factors, such as river flow.

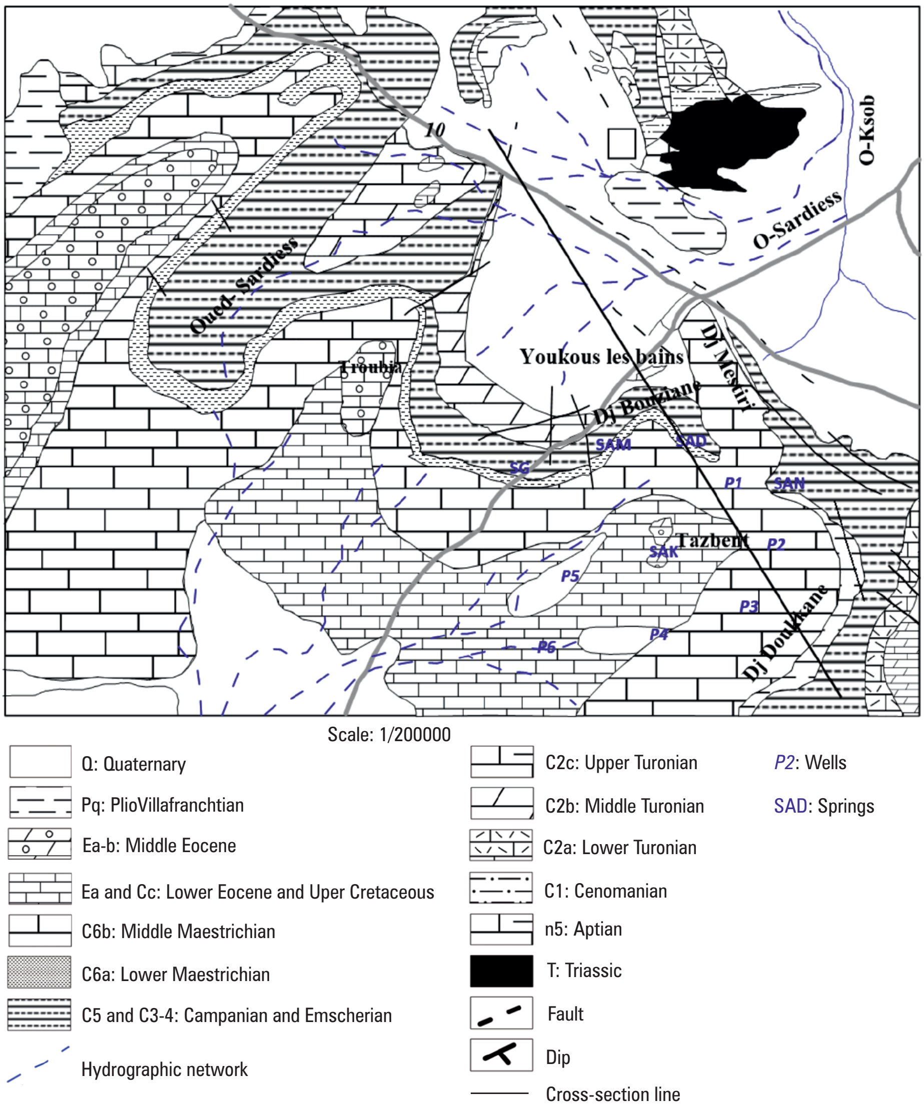

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Fig. 2A. Geological map of the study area

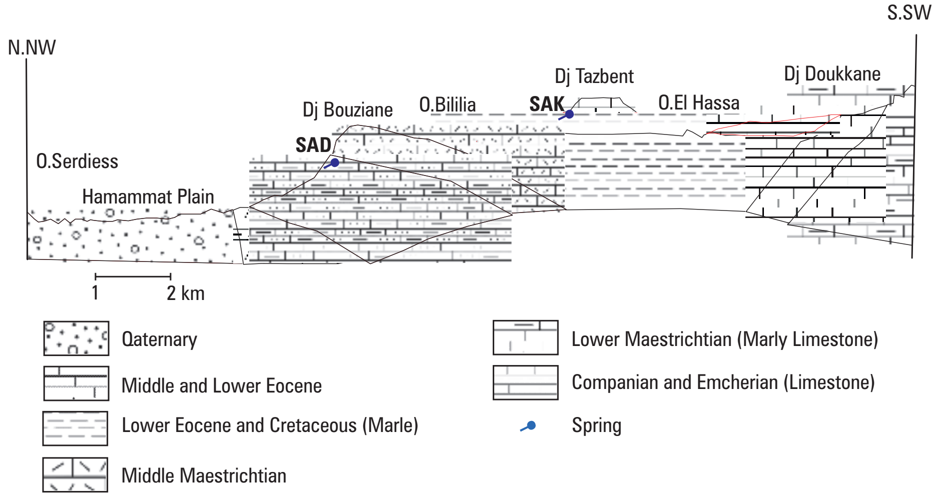

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Fig. 2B. Geological cross-section in the study area

3. Methodology

Four karst springs (Bouakous, Bouakous Wadi, Amacha, and Gaagaa) were monitored and sampled in ten periods (September 2021, October 2021, November 2021, December 2021, January 2022, February 2022, March 2022, April 2022, May 2022, and June 2022).

The temperature, conductivity and pH were measured in the field. Electrical conductivity and water temperature were measured using an Orion 240 conductivity meter. pH was measured using an Orion 250 pH-meter, usually calibrated using two standard buffers.

Chemical analyses were conducted at the hydrochemistry Laboratory of Tébessa University. Major cation concentrations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) together were determined by atomic adsorption spectrophotometry. Calibrations for cation analyses were performed using appropriately adopted standards, and both laboratory and international reference materials were used to check accuracy.

Bicarbonate analysis was performed by titration to the methyl orange endpoint. Concentration of chloride was determined by titration and the precipitation of AgCl until silver chromate appears, While sulphate was determined by the precipitation of $BaSO_4$ followed by the measurement of absorbance with a spectrophotometer.

All samples were filtered by 0.2 μm filters and stored at 4°C in the laboratory. Samples analysed by ICP-MS were acidified with an ultra-pure 1:1 nitric acid (30% HNO_3) mixture after filtration in the field.

The ion balance, saturation index of calcite (*SICalcite*), dolomite (*SIDolomite*), gypsum (*SIGypsum*), and aragonite (*SIAragonite*) in the spring samples were calculated by the PHREEQC [Parkhurst et al. 2015] with the WATEQ4F database.

Stable isotopes of oxygen (δ18O) and deuterium (δ2H) were determined by means of an LGR liquid-water isotope analyzer-DLT 100 (ABB Company, Mountain View, CA, USA) with a precision of < 0.1‰ for δ18O and < 0.3‰ for δ2H. Sampling was carried out in 150-ml glass bottles and analysed in the laboratory of the department of hydrogeology at University of Montpellier in France.

4. Results and discussion

Hydrogeochemical data from the karst springs in the Tezbent Plateau are shown in Table 1. The hydrochemical data were assessed by the PHREEQC [Parkhurst et al. 2015]. The relative analytical error (E%) of the most samples was within an acceptable range of ±5%. The following discussion will demonstrate the significance of these results in the context of groundwater origin, water type, water-rock interaction and the origin of water chemistry.

4.1. Classification of the water

Chemical analysis of studied samples is presented in Table 1. Water samples are classified according to their chemical composition using the Piper diagram [Piper 1944]. This classification is based on the concentration of the four major anions: bicarbonate, sulphate, chloride and nitrate, and on the four major cations: sodium, potassium, calcium and magnesium [Simler 2004].

The Piper diagram in Figure 3 shows that the overall chemical character falls within a fresh groundwater end-member $Ca^{-}HCO_3$ water type with low salinity concentrations. The water type changed continuously due to the influence of many factors:

Table 1. Chemical composition ($mg \cdot l^{-1}$) of groundwater from the study area

Samples	pH	TDS	NO_3^-	HCO_3^-	SO_4^{2-}	Cl^-	Na^+	K^+	Mg^{2+}	Ca^{2+}	Po_4^{2-}
SAD	7.9	407	5.2	194.3	35.25	63.9	80.0	5.7	8.34	89.72	1. 7
SG	7.8	461	6.1	251.5	40.0	65.7	15.5	8.3	11.19	60.92	1.9
SAM	7.9	543	8.8	283.0	49.01	73.2	18.3	9.0	33.38	77.33	1.4
SAN	8.1	481	5.6	243.0	38.22	62.46	16.3	7.43	25.6	82.55	2.1
P1	7.2	784	3.6	212	110.0	88.9	88.0	10.62	54.9	112.2	3.7
P2	7.3	796	7.5	209	102.3	84.98	72.3	11.6	48.55	162.09	0.3
P3	7.4	758	4.3	223	160.8	79.3	65.4	8.6	35.7	157.1	4.8
P4	7.1	815	8.6	211.3	190.0	99.5	60.2	5.34	29.6	106.03	3.2
P5	7.0	1158	6.0	305.23	205.6	139.9	71.34	6.91	67.7	184.52	3.8
P6	7.2	855	7.0	248.6	180.9	91.69	57.2	7.6	39.31	163.23	0.7

First, the water-rock interaction of the aquifer material, and, second, the influence of human activities, such as irrigation return flow and overexploitation of the aquifer system. In result there was a rapid increase in sodium, sulphate and chloride concentrations in the aquifer.

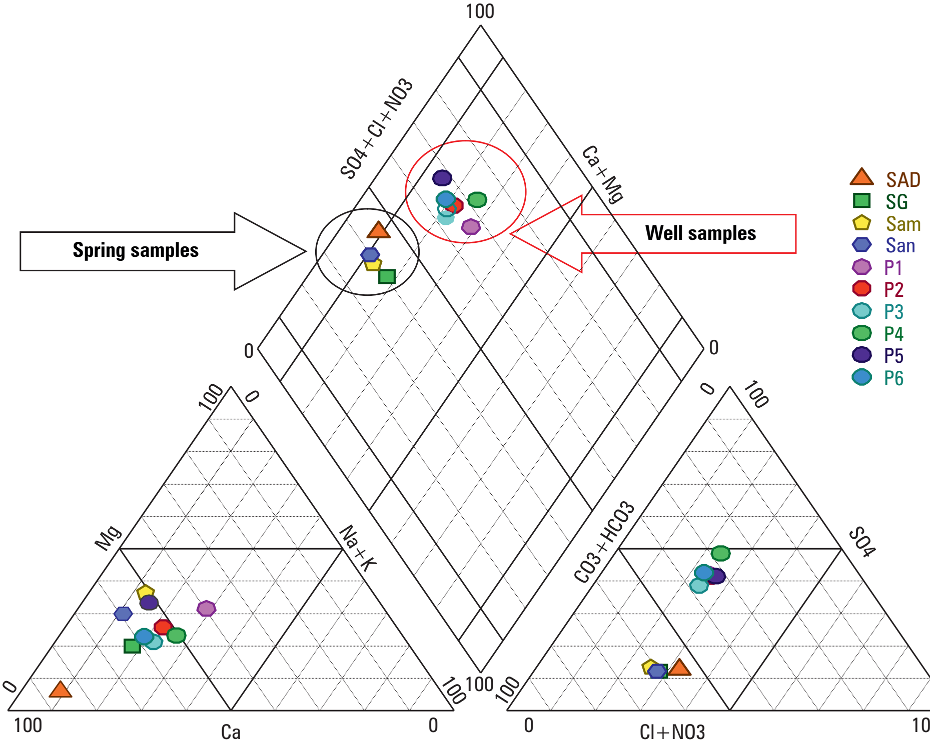

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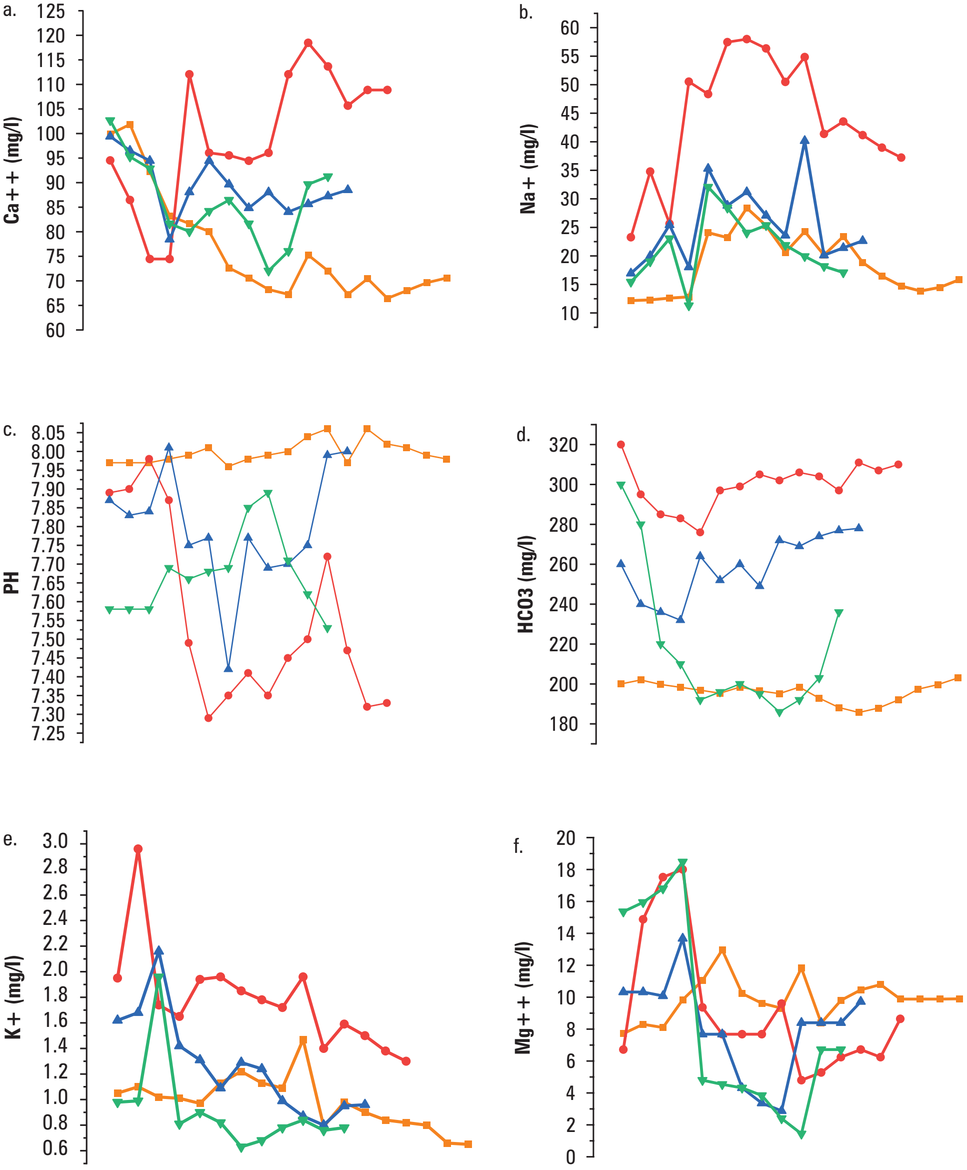
Fig. 3. Piper trilinear diagram of water chemistry in the study area

4.2. Springs hydro-chemograph analysis

Relating to the hydro-chemographs, different interpretations for the studied springs can be proposed (Fig. 4).

The pH of the springs ranges between 7.29 and 8.06 (average 7.77), which indicate neutral or slightly alkaline water (Fig. 4b and Table 1). The variability in pH of the springs is caused by changes in flow paths, water discharge, and residence time within the aquifer [Fehdi 2011]. Two of the springs (Bouakous and Wadi Bouakous) show the same pH values during the Autumn and Winter 2021 precipitation event. The similarity of the pH patterns points to the similarity of the origin of water (same aquifer). The other springs show an increase and variability of pH within the same periods. The pH values of all springs during the spring and summer seasons show a decrease over the time, indicating slightly acidic conditions (Table 1). This is due to the nature of the karst area and the dry climate during this period. Therefore, the temporal variation of the pH value can be used as a tracer in karst waters.



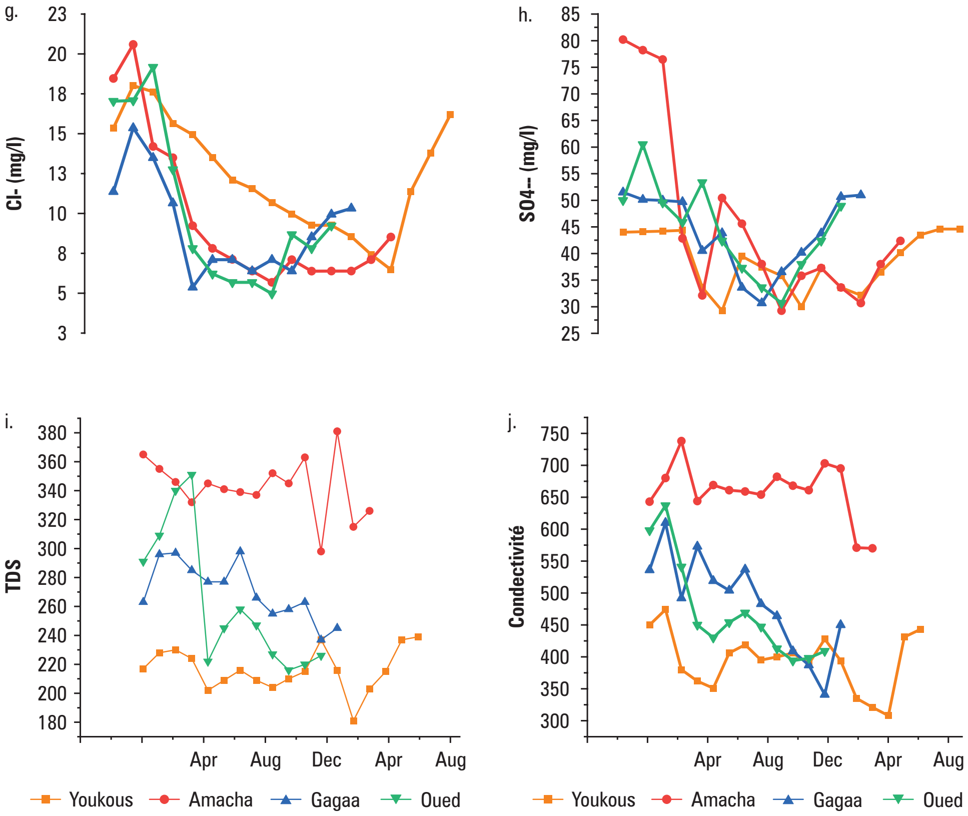


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Fig. 4. Hydro-chemograph of the karst springs in the study area: (**a**) Ca^{2+}; (**b**) Na^{+}; (**c**) pH; (**d**) HCO_3^{-}; (**e**) K^{+}; (**f**) Mg^{2+}; (**g**) Cl^{-}; (**h**) SO_4; (**i**) TDS (mg/l); (**j**) EC (µS/cm)

Electrical conductivity ranges from 321 to 738 µS/cm, highlighting differences in recharge rate and seasonal effects between wet and dry seasons (Fig. 4d). In generally, conductivity decreases during the wet season, reflecting dilution by precipitation water. However, this situation was completely reversed (except for the Amacha spring) in November 2021, when EC increased drastically during dilution by recharge. The dilution processes followed by a piston flow effect are assumed to be the reason of the EC increase during the recharge period.

Temporal variation of major cations (Ca^{2+} and Mg^{2+}) and anions (SO_4^{2-} and HCO_3^{2} $^{-}$) between wet and dry seasons correlates to EC, as illustrated in Figure 4. The calcium chemographs of spring water mainly show a decrease in calcium concentration during recharge periods, except for the Amacha spring (Fig. 4f), which demonstrates the reverse effect (increase in the Ca concentration with a growing recharge during winter season). The observed zigzag-like pattern in the Ca chemographs of all springs in the study area indicates the similarity in recharges and flow systems for both springs.

A time lag was reinforced by the most noticeable changes in hydrogeochemistry after the recharge events. This time lag suggests the presence of piston phenomena [Fehdi 2011].

Sulphate concentrations show the same variation as Ca corresponding to the dilution with recharge water, except in the Amacha spring, which follows the opposite patterns (Fig. 4h). The sulphate concentration was higher during the Autumn 2021, especially for the Amacha spring. Sulphate-rich waters may form by oxidation of pyrite in carbonate rocks [Fehdi 2008]. Oxidation of pyrite concretions and gypsum impurities along the flow path of Tezbent karst aquifer leads to formation of water rich in sulphate. The direct response of sulphate to the recharge is interpreted as the presence of conduit-type flow and is reported from various karst springs worldwide.

4.3. Water-rock interaction and geochemical processes

The hydrochemical variations in water serve as valuable indicators, providing insights into water-rock interactions and geochemical processes of the groundwater flow [Fehdi et al. 2014]. The observed chemical characteristics of groundwater in the Hammamet plain are primarily attributed to interactions between groundwater and the surrounding host rocks [Fehdi 2008]. To survey these processes, it is necessary to describe the average mineral composition of the rocks that host water and identify the chemical reactions that drive the geochemical evolution of groundwater [Salameh 2001]. Typically, these reactions include chemical weathering of rock-forming minerals, dissolution-precipitation of secondary carbonates, and ion exchange between water and clay minerals [Fehdi 2008].

The resolution of hydrogeochemical interactions typically involves two approaches: mathematical and graphical. The mathematical approach is commonly employed to calculate saturation indices, which provide insight into the equilibrium state between groundwater and the surrounding mineral rock assemblage [Bakalowicz 2005].

Calculation of various parameters, such as pH equilibrium, pCo_2, ionic strength, and saturation indices for minerals, such as calcite, aragonite, dolomite, gypsum, and anhydrite, gives a thorough understanding of the chemical dynamics [Todd 1980].

Calculated saturation indices (Table 2) show that all springs are over-saturated ($SI \geq 0.05$) with respect to calcite and aragonite, indicating a longer flow path and residence time in the aquifer. With regard to the *SI Dolomite*, only the Bouakous and Gaagaa springs were in an oversaturated state, while the rest were undersaturated with respect to dolomite. All springs were undersaturated with respect to gypsum and anhydrite. Dissolution is considered to be incongruent when one mineral dissolves while another is oversaturated and thus precipitates.

Table 2. Saturation indices of groundwater samples

Groundwater samples	SI Calcite	SI Aragonite	SI Dolomite	SI Gypse	SI Anhydrite
SAD	0.32	0.17	–0.95	–1.79	–2.01
SG	0.22	0.07	–0.48	–1.90	–2.12
SAM	0.22	0.07	–0.13	–1.74	–1.96
SAN	0.30	0.15	–0.12	–1.81	–2.03
P1	0.12	–0.02	–0.27	–1.01	–1.23
P2	0.21	–0.35	–1.14	–0.88	–1.10
P3	0.03	–0.13	–0.82	–0.93	–1.15
P4	–0.06	–0.20	–0.87	–0.89	–1.11
P5	0.29	0.14	–0.03	–0.61	–0.83
P6	–0.12	–0.27	–1.07	–0.80	–1.02

4.4. Origin and recharge mechanism of groundwater

Stable isotopes of oxygen and hydrogen in groundwater of an active hydrological cycle reflect the initial isotopic composition of the recharge rainwater. $\delta^{18}O$ and $\delta^{2}H$ can be used to identify a meteoric line, the slope of which is characteristic of a particular hydrological system [Appelo et al. 1990].

In this work, $\delta^{18}O$ and $\delta^{2}H$ are used to establish the local meteoric water lines, are obtained from the Global Network for Isotopes in Precipitation database managed by the AIEA (The International Atomic Energy Agency), for a period of 6 years (September 1992–December 1998) for the Tunis-Carthage and Sfax meteorological stations (Tunisia) [Celle-Jeonatan et al. 2001].

4.4.1. Groundwater isotopic signatures

Stable isotope compositions of water collected from wells and springs are presented in Table 3. Stable isotope values showed a variation between –8.26 and –7.15 in O^{18} with a mean of –7.861±0.2‰ (n = 10), and between –55.47 and –47.44 in H^{2} with a mean of –51.51 ±0.15‰ (n = 10).

The $\delta^{18}O$ and $\delta^{2}H$ contents for all the investigated groundwater samples are plotted in the classical O^{18}–H^{2} diagram, together with the global meteoric water line ($\delta^{2}H = 8\ \delta^{18}O + 10$), defined by Craig (1961) and the local meteoric water lines (Tunis and Sfax) .

Figure 5 shows that nearly all of the groundwater samples are plotted close to the Tunis and Sfax meteoric line. No significant isotopic modifications by evaporation were indicated, which means that the recharge of the aquifer is quite fast, and the recharging meteoric water does not occupy the soil zone of the recharge area for a long time.

Table 3. Isotopic composition of groundwater from the study area

Samples	Wells and springs	Altitude (m)	δ H^2	δ O^{18}
1	P1	1254	–52.98	–8.26
2	P2	1273	–49.83	–7.23
3	P3	1258	–55.47	–8.23
4	P4	1206	–51.61	–7.71
5	P5	1187	–47.44	–7.15
6	SAD	1230	–51.75	–7.99
7	SG	1210	–52.92	–8.2
8	SAM	998	–51.05	–7.88
9	SAN	1122	–52.93	–8.2
10	SAK	1350	–49.11	–7.76

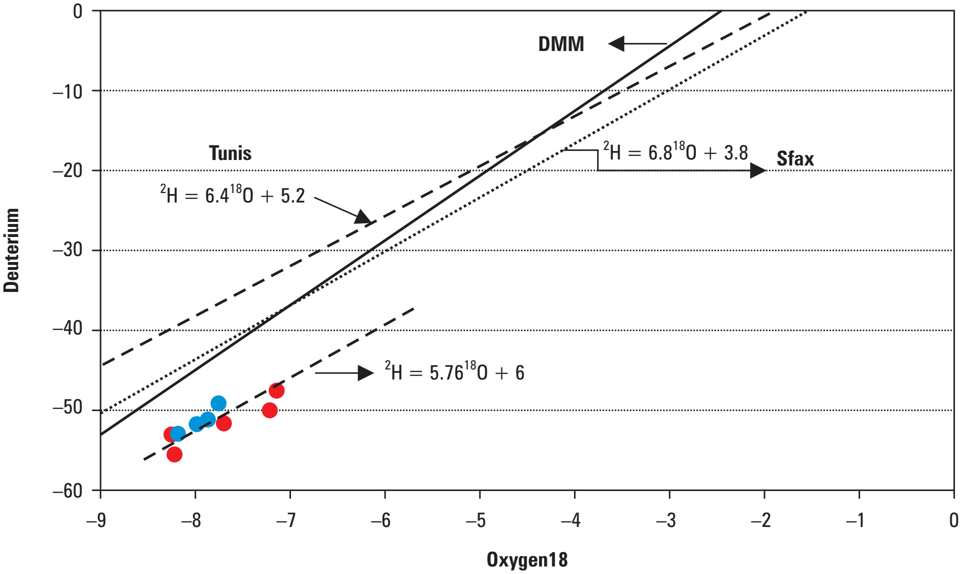

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Fig. 5. δ^2H vs $\delta^{18}O$ relationship in groundwater in the study area. Red circles: spring samples, blue circles: well samples

The similarity of δ^2H and $\delta^{18}O$ for both wells and spring groundwater samples is not surprising in karst regions and it suggests a rapid recharge (fast infiltration process) of groundwater by precipitation throughout highly karst carbonate at high altitudes. This also proves a meteoric origin of groundwater [Araguas and Diaz Teijeiro 2005]. The surplus of deuterium indicates that the study area is recharged by locally generated atmospheric water vapour, reflecting low evaporation rates.

5. Conclusion

In the present study, the sampled springs and wells on the Tezbent Plateau were characterised in terms of hydrogeological and hydrogeochemical composition, which allowed us to propose it conceptual underground flow systems. Water wells, characterising groundwater circulation at shallow depths, are moderately to highly mineralised waters of the Na-HCO_3 type. In contrast to the shallow environment, the CO_2-rich, deeper waters are of the Ca–HCO_3 type, and undergo significant changes in the baseline chemistry along flow lines with increasing residence time.

Two hydrogeological systems were determined in the study area: (1) a deep water system, which is related to extensive and deep circulation of meteoric water in the regional flow system, where the influence of shallow waters is relatively small, and (2) a shallow system, which is related to shallow circulation, and is affected very rapidly by recent rainfall events.

All the underground flow systems are fed by meteoric water. The studied water samples collected from springs and wells are supplied by recharge at the highest levels.

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