

Chemical and isotopic characterization of the thermal waters of Hammam Skhouna Algeria

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Received date: Apr. 28, 2018; accepted date: Dec. 15, 2018

Abstract

A series of chemical and isotopic analyses (O-18 and H-2) of aquifers performed in the Hammam Sokhna area, a large sedimentary basin located in southern Setif, filled with Mio-Plio-Quaternary deposits, which rest on Jurassic and Cretaceous limestones, show that the superficial water table made up of thermal waters regroups waters with the most impoverished isotopic signatures. The recharge is ensured by meteoric water with an altitude effect. The recharge of groundwater moving in carbonate, karstified formations is ensured by meteoric water that underwent a slight evaporitic loss. The binary diagrams show that the water mineralisation is controlled by mineral dissolution-precipitation processes and by cation exchange.

Keywords: springs; hydrochemistry; recharge; isotope; Algeria.

1. Introduction

The Hammam Sokhna thermal springs are an entity of the Setif southern upper plains of oriental Algeria, located between latitude 35°58' north and longitude 5°50' east. The climate is semiarid; the annual mean rainfall is of 400 mm/y. The air annual mean temperature is of 13.5 °C [1]. This is a peneplain of a mean altitude of 870 m, characterized by the presence of two salty lakes, El Baida and Sebkha Sokhna; located south and north of the Hammam Sokhna village.

It is subject to the influences of Mediterranean and the Tell Atlas air current in the north and those of the Saharan Atlas in the south. This sedimentary set is constituted of carbonate karstified formations of Jurassic and Cretaceous at the base, the calcareous outcrops of which are visible in the Djebel Tnouit and its continuation Djebel Chebka in the north, Djebel Fartas in the east, Djebel Agmeroual to the south and are surmounted by a Plio-Quaternary filling with varied particle-size texture.

This aquifer system would be the center of two water tables, one is superficial, shallow marked by moderately mineralized cold water 1238 mg/l, the other is deep, characterised by hot water with excessive mineralization, with a mean of 2453 mg/l. The Cretaceous aquifer, from which the Hammam Sokhna thermal springs emerge, has a mean temperature of 43, 78 °C.

The aim of this paper is to define the chemical and isotopic signature of the Hammam Sokhna thermal springs in order to distinguish the origin of salinity and of water recharge.

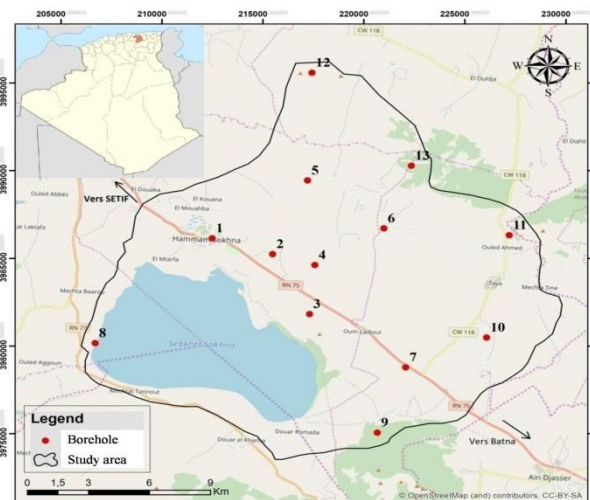


Figure 1. Geographical location of the study area.

2. Experimental details

2.1. Geological setting

Geology The Hammam Sokhna area belongs to the southern Setif domain where carbonate formations of Jurassic and Cretaceous outcrop [2]. In the north, we have Djebel Tnouit, in the south Djebel Messaouda and Rohnia, and in the west Djebel Tella. Many saliferous Triassic outcrops are also present across the terrain. The center of the plain is marked by two terrains: Quaternary and Mio-Pliocene [2], (Fig. 2). Quaternary is made up of salty soils periodically floodable, consisted of mud, ancient alluvia and slope formations. Mio-Pliocene is made up of lacustrine limestones, conglomerates and Villafranchian

marls that are well represented in the north of the spring. There are also sands, gravel, conglomerates, silt and red clay to gypsum. The structural analysis of the Setif area lets appear several tectonic stages, but it is the last, post-tortonian that is responsible for the present orography [2]. It resulted in the filling up of Mio-Pliocene basin recharged by sediments from dismantling of surrounding relief sowing to previous stages of compression and tension [1].

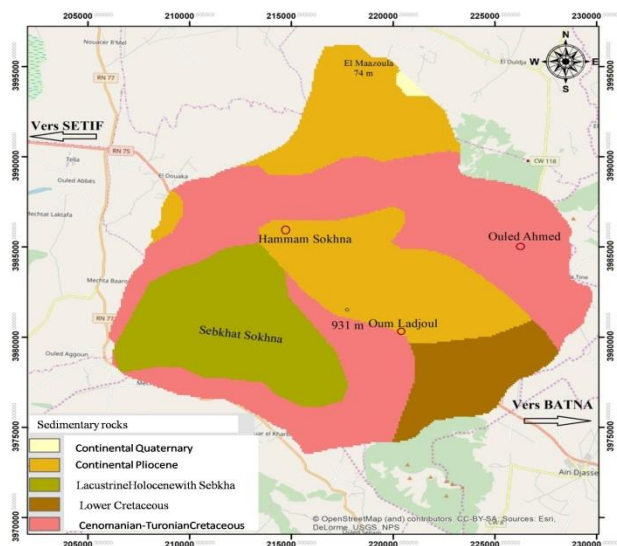


Figure 2. Geological map of the Hammam Sokhna area

Several hydrogeological studies carried out in the area [1, 3, 4] allow highlighting two large types of aquifers. The first superficial aquifer is of interstices porosity type and lies in the Mio-Plio-Quaternary formations. The second aquifer lies in the Jurassic and Cretaceous carbonate karstified formations. The two aquifers are separated by a thick impervious clay layer of Miocene. The presence of the Triassic outcrop 6 Km far from the spa is to be noted. The diverse spas located in the Hammam Sokhna area are supplied by seven boreholes, the depth of which ranges between 60 and 120 m and their operation capacity ranges between 5 and 10 l.s-1. The study of borehole cuttings showed the existence of a first layer consisted of clays, alluvia and mud up to a depth of 32 m. From this elevation, we see a second more resistant layer, consisted of cracked and karstified lacustrine limestones. Five boreholes capture freshwater at depths varying between 150 and 301 m. The completion of boreholes in these carbonate formations enabled to detect the presence of cavities, indicating the existence of a well-developed endokarst [1].

2.2. Materials and methods :

For the characteristic study of water, 13 samples were collected from the Hammam Sokhna during the period of May 2017, in which hot water emerges in a large Plio-Quaternary plain through a fault [1]. There are three vents surrounded by the El Baida Chott in the south and the Sebkhia Sokhna in the north.

Temperature, pH and electrical conductivity were systematically measured in situ with a handled multi-parameter [5, 6].

The sampled water was object of a chemical analysis of major elements (Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , Cl^{-} , SO_4^{2-} , HCO_3^{-} and NO_3^{-}) and of stable isotopes of the water molecule ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) that were performed in the laboratory of isotopic hydrology of the atomic research center of Algiers (CRNA). The findings of these analyses were reported on Table 1.

Table 1: Chemical and isotopic composition of the Hammam Sokhna area water

No	T°C	pH	EC $\mu\text{S}/\text{cm}$	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}	NO_3^{-}
1	16	7,1	1030	72,57	36,6	95	2	160	50	274,5	7
2	43	7,21	3680	206,4	58,57	505	12	930	350	280,6	0
3	43	7,07	5060	291,6	77,05	664	14	0	500	274,5	0
4	45	7,12	3440	119,28	55,9	456	11	800	330	286,7	11
5	45	7,24	3430	187,6	57,83	463	11	800	330	286,7	11
6	43	7,84	3240	111,72	49,06	444	11	700	380	268,4	0
7	43	7,6	3930	323,6	38,59	449	11	0	380	298,9	0
8	44,5	7,14	3490	197,4	59,15	464	11	800	430	256,2	0
9	21	7,4	1830	129	57,03	171	5	275	248	305	7
10	17	7,54	1690	111,2	62,92	146	3	210	294	298,9	5
11	25	7,68	1050	76,54	32,8	100	4	135	158	225,7	8
12	21	7,24	1190	114,6	34,47	93	1	170	114	237,9	53

The sampling campaign was performed during the period between November and December 2016. Certain measures were carried out onsite in order to determine the physicochemical parameters values evolving quickly after sampling, such as temperature, pH and electrical conductivity by means of multi-parameter probe, whereas the chemical analyses of determined major elements were carried out at le Laboratoire de l'Agence Nationale des Ressources Hydriques (ANRH) of Khenchela. The tab 1 contains the analyses findings.

3. Results and discussion

3.1. Hydrochemistry

Temperatures of all sampled waters are comprised between 16 and 25°C for cold water of Jurassic and Cretaceous aquifers, with a mean value of 20°C. For the boreholes of hot water of the aquifer of Plio-Quaternary filling, temperatures are comprised between 43 and 45°C, with a mean value of 44°C. Electrical conductivity measured for all waters ranges from 1030 to 5060 $\mu\text{S}/\text{cm}$, with a mean around 2725 $\mu\text{S}/\text{cm}$. For hot water it is of 3701 $\mu\text{S}/\text{cm}$ on average, and of 1358 $\mu\text{S}/\text{cm}$ for cold water. It should be noted that the Sebkhia water has a conductivity of 74000 $\mu\text{S}/\text{cm}$.

The most mineralized thermal springs are in immediate relation with gypso-saline sediments of Triassic, very spread in Algeria [1], so the values indicate that the Hammam Sokhna's water is mineralized and would have crossed the gypso-saliferous Triassic terrains.

The findings of chemical analyses for major ions expressed in (mg/l) are reported on Piper diagram (Fig. 3) that shows that the Hammam Sokhna area water evolves from sulphate -calcium pole to a major facies of sulphate -sodium type in the Hammam Sokhna center.

3.2. Salinisation mechanism and mineralisation acquisition

The salinity origin of alluvial groundwater and its geochemical characteristics were approached by chloride (Cl) and sodium (Na), regarded as good salinity tracers. Since seawater intrusion is regarded as the main origin of salinity of alluvial groundwater, the relation Na vs. Cl (Fig. 4) should indicate a linear relation characterizing a mixture between the freshwater/seawater bodies.

In order to better distinguish the Salinization processes of groundwater, we used the crossed diagrams of major elements with chlorine ion concentrations. This latter is a conserved element, does not contribute to water-rock interaction, characterizes the origin of water salinity and constitutes a mixing tracer [7]. The disposition of the different water points analyzed with respect to the freshwater-saltwater (rainwater-seawater) mixing line can be of great significance to identify other phenomena responsible for water mineralization and for mixing process additives [7].

In carbonate aquifers, the simultaneous Ca^{2+} -enrichment and Mg^{2+} impoverishment are essentially explained by water-rock interaction as dolomitisation, dissolution and precipitation. The Ca^{2+} - Mg^{2+} -exchange reaction by dolomitisation was reported as a main cause of the decrease of Mg/Ca ratio [8], the Mg/Ca ratio in our case is very low and confirms the assumption stated above. Given that Na^+ content should balance Cl- content on the diagram Na^+ and Cl-, the totality of points lie below the freshwater-saltwater line, thereby showing an Na^+ deficit.

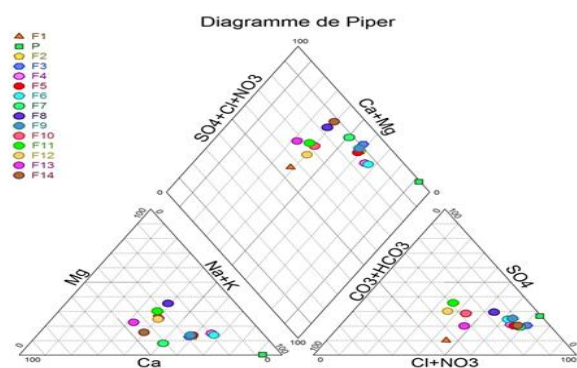


Figure 3. Piper diagram showing the chemical compositions of sampled water

Na^+ impoverishment and Ca^{2+} -intake are the attributes of the reverse ion base exchange phenomena that occur in aquifers. Na^+ is fixed by the host rock thus

releasing Ca^{2+} [9, 10], which is consistent with the Ca^{2+} versus Cl-diagram showing that the points are above the freshwater-saltwater mixing line [9, 11]. The SO_4^{2-} -Cl- relation shows that the majority of the points lie above the freshwater-saltwater line. The sulfates ions enrichment has its origin in the dissolution of gypsum by leaching of evaporites and by a secondary salinization by irrigation return flows loaded with salts at the time of dilution, or from contamination by pollutants deriving from farmlands in shallow and high-permeability aquifers [9, 11].

The relation between K^+ and Cl- is marked by K^+ impoverishment and confirms the assumption of alkali adsorption by the CEC [10].

3.3. Mineralisation highlighting

The relation between K^+ and Cl- is marked by K^+ impoverishment and confirms the assumption of alkali adsorption by the CEC [11]. The dissolution of a mineral in water can be described by a balance state, when water is in contact with a mineral, the solution concentration increases to reach a maximum for given physicochemical conditions. So, the solution is said to be saturated in this mineral.

The saturation state is expressed by the saturation index:

$$SI = \log(K) - \log(IP)$$

With K the balance constant and IP the ion product.

The saturation index expresses the chemical balance degree between water and the mineral in the aquifer matrix, considered as a measure of the process dissolution and/or precipitation regarding the water-rock interaction [12,13,14].

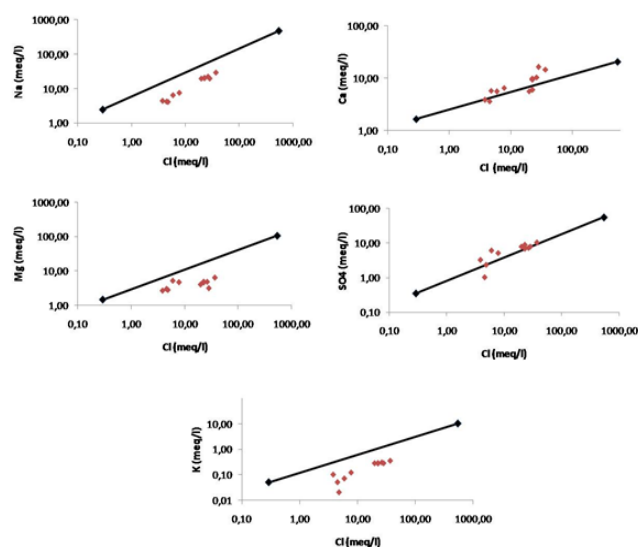


Figure 4. Binary diagram

Three cases are possible:

$SI < 0$ signifies an undersaturation of a solution with respect to a mineral;

$SI = 0$ indicates a saturation state;

$SI > 0$ shows a supersaturation.

The use of PHREEQ, integrated in the diagram program of hydrochemical [15] computations allowed us to calculate the saturation index of anhydrite, aragonite,

calcite, dolomite, gypsum and halite. The significant results of all groundwater samples analysed (Fig. 5) show that this water is saturated with respect to calcite, aragonite and dolomite, and undersaturated with respect to halite, anhydrite and gypsum. The computation of saturation indices of minerals in water indicates that carbonate minerals tend to precipitate under the form of calcite and dolomite. In contrast, the evaporitic minerals (gypsum and halite) tend to dissolution.

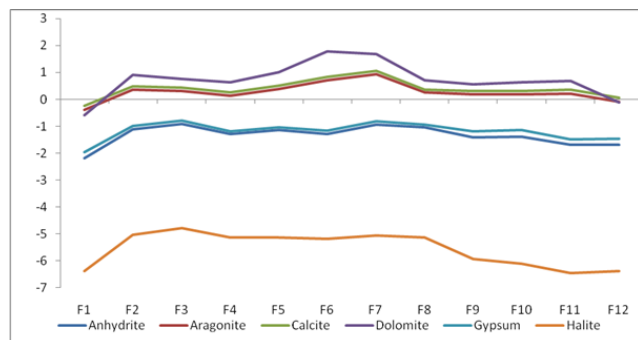


Figure 5. Saturation indices of solution minerals balance.

3.4. Principal component analysis :

In order to define the relation linking the different parameters between each other on the one hand, and to identify the water types having the same characteristics on the other hand, we have performed a principal component analysis (PCA) for all water located at different depth horizons, applied to quantitative variables (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^-), the physicochemical parameters (temperature, conductivity, pH) and the individuals (boreholes).

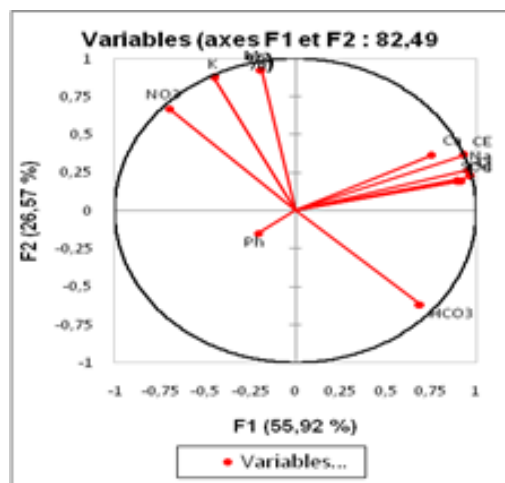


Figure 6. Analysis within the variables.

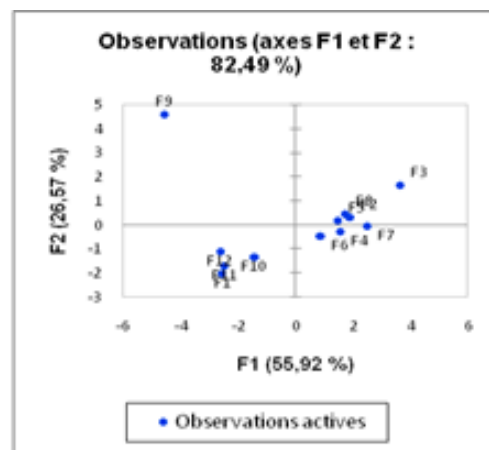


Figure 7. Individual projection of hamamSokhna water's.

The study of eigenvalues spectrum shows that there are two axes to be retained for the interpretation of findings because they hold 82, 49 % of the total inertia. The axis F1, defines 55.92% of the explained variance, in the variables space it appears as a mineralization factor (Fig. 6 , Fig. 7), it regroups the salinity elements (EC , and Ca^{2+} , Na^+ , Cl^- , Mg^{2+} and SO_4^{2-} contents). The inertia axis F2, representing 26, 56 % of information, is positively defined by Mg , K , NO_3 , EC , and Ca , and negatively by bicarbonates; this is an opposition between highly mineralized hot water, with relatively highly values of dry residue, in relation to Plio-Quaternary aquifer versus low mineralization deep cold water of Jurassic and Cretaceous aquifer.

3.5. Isotopic hydrology :

The isotopic composition of groundwater has a large range of variation considering the depth of captured water and the lithologic variation of the aquifer formation. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ contents range between -8.80 and -8.71 ‰, respectively with a mean of -8.10 ‰ vs SMOW and between -59.50 and -43.60 ‰ vs SMOW, around a mean of -55.84 ‰ vs SMOW.

The values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ contents, roughly distributed in to two groups corresponding to poor compositions relatively rich in stable isotopes, clearly allow distinguishing two types of water of different origins and horizons, thereby indicating the heterogeneity of water bodies recharging the aquifer. The most enriched values are recorded at the DjebelsTnount and Chebka boreholes, from which emerges low temperature cold water, whereas the most impoverished values are measured on hot water, recorded on the ARAB and MGHU boreholes.

The isotopic composition of hot water exhibits $\delta^{18}\text{O}$ and $\delta^2\text{H}$ contents ranging between -8.89 and -8.71 ‰ vs SMOW, respectively, with a mean of -8.82 ‰ vs SMOW and between -59.5 and -58.7 ‰ vs SMOW, and around a mean of -58.97 ‰ vs SMOW. The isotopic composition of low temperature water exhibits $\delta^{18}\text{O}$ and $\delta^2\text{H}$ contents ranging between -8.46 and -5.71 ‰ vs SMOW, respectively, with a mean of -7.26 ‰ vs SMOW and

between -55.9 and -37.7 ‰ vs SMOW and around a mean value of -49.16 ‰ vs SMOW.

The (Fig. 8) shows that the boreholes capturing deep most evaporated groundwater, are different from those of the boreholes capturing hot groundwater. The correlation between the different points allows obtaining the evaporation line of groundwater having a slope of 6.21, different from that of global meteoric water. These enriched values can also reflect an intake by a recent recharge from external zone to the study area in favour of a cracked or even karstified medium.

Thermal water lies close to the global meteoric water line [16], thus indicating meteoric water without an isotopic process and without any paleoclimatic effect [17]. However, low deuterium excess ranging between 10.88 and 12.34 can be explained by an influence of Mediterranean precipitations [18, 19].

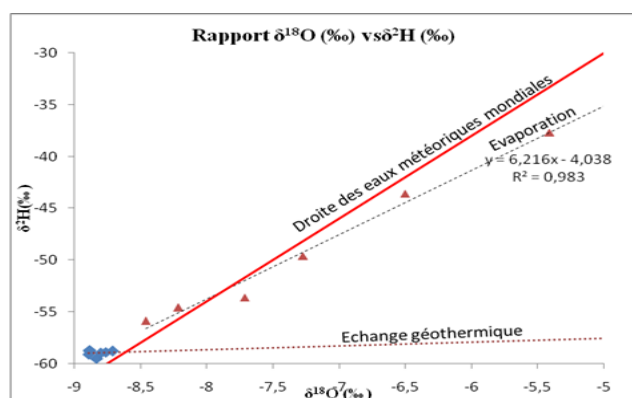


Figure 8. Relation between $\delta^2\text{H}$ contents (‰) and $\delta^{18}\text{O}$ contents (‰) (June 2017) for the Hammam Sokhna groundwater

4. Conclusion

The use of geochemical techniques shows that the Hammam Sokhna area water evolves from sulphate-calcium pole toward a major facies of sulphate-sodium type at the Hammam Sokhna center, and the mechanisms giving rise to the mineralization and to the evolution of water chemical facies are water-rock interaction occurring along the runoff in the reservoir, the cation exchange and the percolation of irrigation water loaded with salts and fertilizers in irrigated lands.

The use of isotopic tool reveals that the boreholes capturing the deep, most evaporated water table are different from the boreholes capturing superficial hot groundwater. The correlation between the diverse points allows obtaining the evaporation line of groundwater exhibiting a slope of 6.21, different from that of global meteoric water. These enriched values can also reflect an intake by a recent recharge from an external zone to the study area in favour of a cracked or even karstified medium.

The location of thermal water in the vicinity of global meteoric water line is indicative of meteoric origin without

an isotopic process and without any paleoclimatic effect. However, a low excess of deuterium, fluctuating between 10.88 and 12.34, can be explained by an impact of Mediterranean precipitations.

Acknowledgements

The authors are pleased to Abbes Laghrour University for providing the facilities for the research.

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