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### RESEARCH ARTICLE

## HYDROCHEMICAL QUALITY OF SPRINGS IN MAHOUNA MASSIF, GUELMA, NORTH-EAST OF ALGERIA.

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#### Abstract

The hydrochemistry of springs in Mahouna massif, located at Guelma, north east of Algeria was evaluated for drinking water and irrigation. Ten major springs were sampled. The physical parameters (pH), Electric Conductivity (EC), Total Dissolved Solids (TDS), TH as well as the concentrations in major ions  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Fe}^{2+}$  and  $\text{NO}_3^-$  analyzed by standard methods. Two chemical facies are predominant in the study area (Na-Cl and Ca+Mg- $\text{HCO}_3$ ). Water-rock interaction characterized by the dissolution of carbonates and silicates plays a primordial role in the chemical composition of the groundwater. The hydrochemical study of the area showed that the majority of cations and anions, electric conductivity, the TDS and the TH which characterize the chemical composition of the water springs are above the limits allowed for the drinking water according to standards. SAR, SS<sup>°</sup>P and RSC reveal that, barring a few locations, most of the groundwater samples are safe for irrigation purposes.

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#### Introduction:-

In the study area, Water resources have become increasingly limited and difficult to exploit by water resources have become increasingly limited, difficult to exploit by drilling because of the rugged terrain and shows the very steep slopes. Springs are natural emergence that appear to the surface. They are natural drainage or one-off outlets of groundwater. In the worldwide, the emergences are captured to satisfy for water supply (Bourlier et al., 2005; Karakaya, 2006; Omar, 2008). In the Massif of Mahouna located south of Guelma, natural springs are the main points of access to water resources for rural populations. These sources are sustainable and water flow is between 2 to 10 l / s. From a hydro geological point of view, they represent a potential supply of drinking water to populations and meet the demand for irrigation water and livestock. The purpose is to evaluate the present status of water quality in the area for human consumption and irrigation uses

#### Material and Methods:-

##### Study area:-

The study area is belonging to Guelma district and located in the north-eastern part of Algeria (Fig. 1). Many springs emerge in this locality and its water contributes in drinking purposes and irrigation of the communities and farmers of the area. The study area is characterized by an elevation of about 755 to 1110 m above the sea. The

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outcrops are occupied by the mastic, cork oak, blueberry, myrtle and olives trees. The most important economic activity of the area is agriculture. The climate of the study area is considered to be semi tempered, the annual average precipitation being approximately 555 mm. Rainfall occurs from august to June, with a maximum during January and February of each year. The average temperature is approximately 9°C in winter and 27°C in summer, though summer high temperature can reach 35°C in July. Annual total evaporation rises to 919.43 mm. Geologically, the surface of the study area is rather simple. It is made up of a series of alternating elongated ridges, hills and plateaus. The ridges consist of clayey sandstone rich with quartzite bedded on clay referred to as Numidian formations (Numidian aquifer) and Tellian carbonates bedded on marl (carbonate aquifer), (Vila, 1980; Chouabbi 1987). Structurally, the Numidian formations are carried on limestones and occupied the upper position. The aquifers are mainly recharged by precipitation; secondarily by the Infiltration of water from faults is another possible source of aquifers recharge.

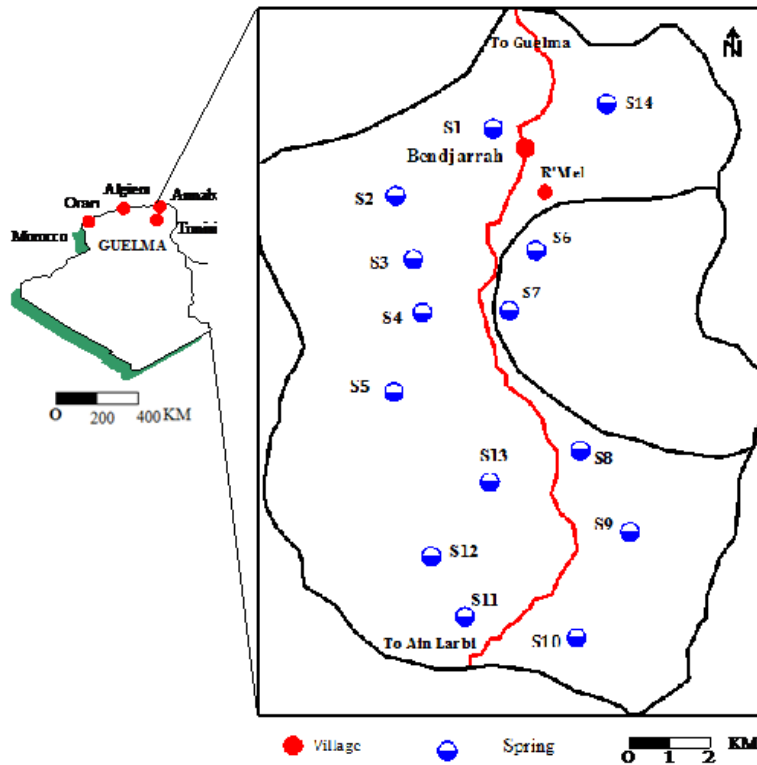


Fig 1:- Location of the study area in eastern part of Algeria

#### Sampling analysis:-

Ten major springs were assigned for sampling campaign (figure1). They were collected into new 1.1 polyethylene bottles that had been rinsed two or three times with the water to be analyzed. The bottles were filled until overflowing and closed underwater to minimize aeration. All bottles were carefully labeled and numbered prior to transport and kept at low temperature 4 C. Physico-chemical parameters (temperature, pH, and EC) were measured in situ using a multi-parameter WTW, and dissolved oxygen was analyzed with device multiline P3PH/LF-SET with a selective probe (WTW). Alkalinity was determined using volumetric titration with sulfuric acid 50.1N-. The cations ( $\text{Na}^+$  and  $\text{K}^+$ ) were carried up by flame spectrophotometric absorption. Ca and TH were determined by the titrimetry method using Eriochrome and Murexide as indicators. A spectrophotometer UV-visible spectral photolab WTW with compatible kits is used to analyze anions  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and metal ( $\text{Fe}^{3+}$ ). Analyses have been accomplished at Civil Engineering and Hydraulic Laboratory in University of Guelma. The results of hydrochemical analysis were compared to WHO standards (2011) standards for the suitability evaluation of the water springs for drinking and domestic uses. To study the water quality for irrigation, sodium adsorption ratio (SAR), the percentage of sodium, and residual sodium carbonate (RSC), magnesium ratio, and Kelly's ratio were calculated.

## Results and discussion:-

### Water chemistry:-

The samples were collected from 10 springs from the Mahouna Massif during the stage period (April 2016). The analytic results for each parameter and minimum, maximum, average and standard deviation are summarized in Tables 1 and 2.

**Table 1:** -Hydrochemical results of the springs

ID	TDS	pH	O2	EC	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Fe <sup>2+</sup>	Cl <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub>	SiO2
S1	668	7.65	6.10	1,120	56	12	154	6	6	225	86	4	13.25
S2	595	7.58	5.57	1,021	68	17	125	3	4.5	210	58	3.41	11
S3	595	7.42	5.29	848	87	36	48	2	2	100	50	10	6.25
S4	632	7.36	6.10	891	90	38	56	1.25	1.25	98	52	15	5.45
S5	624	7.60	5	1,061	65	15.60	136	5	3.20	215	48	21	8.98
S6	631	7.7	6.25	1,105	62	22	146	1.2	2	245	33	7	9.23
S7	654	7.72	5.32	1,129	53	12	163	4.25	1.32	256	36	9	12.02
S8	580	7.65	6.37	995	56	12	112	2	3.12	235	46.5	2	7.33
S9	610	7.73	6.15	1,061	60	13	145	3.2	3	228	39	10	5.66
S10	527	7.53	5.66	700	72	27	24	2	2.32	79	22	25	9.63

**Table 2:-** Minimum maximum, averga and SD

Variable	Minimum	Maximum	Mean	SD
TDS	558	664	613.30	32.79
pH	7.36	7.73	7.59	0.13
O2	500	6.37	5.78	0.47
EC	818	1,145	1,018.20	120.23
Ca	53	90	67.20	12.64
Mg	12	38	21.26	9.65
Na	48	163	114.30	44.03
K	1.20	6	2.99	1.63
Fe	1.25	6	2.87	1.47
HCO	89	272	142.10	72.46
Cl	98	256	191.00	65.08
SO4	33	86	49.65	14.87
NO3	2	25	10.64	7.60
SiO2	5.45	13.25	8.88	2.70

Waters samples in the study area are generally alkaline in nature with pH ranging from 7.36 to 7.73 with an average of 7.59 (Table 1). The waters samples are moderately oxygenated, with values oscillating between 5 and 6.37. Electrical conductivity reflects the capacity of water to conduct electrical current, and is directly related to the concentration of salts dissolved in water. EC ranges from 818 to 1,145  $\mu\text{S}/\text{cm}$  with an average of 1,018.20  $\mu\text{S}/\text{cm}$ . According to the analytical data, all the groundwater investigated can be classified into two groups. Group A, by far the most important one is representative of most springs which emerge from Numidian sandstones. The second group comprises especially the water samples from the carbonate aquifer. (Fig.1). The first and the second group waters samples are low in mineralization. The total dissolved solids (TDS) vary from 558 to 664 mg/l (Table 1), the average value being of  $613.30 \pm 32.78$  mg/l. Among the major cations (Fig. 3), a predominance of Na followed by Ca, Mg and K is observed for the first group of groundwater. Concentrations of both Na<sup>+</sup> and Ca<sup>2+</sup> (in mg/l) represent on average 36 and 33% of all the cations, respectively. Mg-K ions are secondary in importance, representing on average 31% of all cations. Among the major anions (Fig. 3), Cl<sup>-</sup> generally dominates, representing on average 55% of all the anions followed by HCO<sub>3</sub><sup>-</sup>, however, the plot of some groundwater samples towards the Cl-NO<sub>3</sub>, and dominant field (Fig. 3) indicates that several springs contain groundwater with insignificant amounts of NO<sub>3</sub> (Table 1). SO<sub>4</sub><sup>2-</sup> ions are less abundant; they represent on average 21 and 20% of all the anions, respectively. In contrast to this, the predominant anion trend is in the order HCO<sub>3</sub><sup>-</sup> > Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > NO<sub>3</sub><sup>-</sup> in the spring S5 and S8 and in cations, the order is Ca<sup>2+</sup> > Mg<sup>2+</sup> > Na<sup>+</sup> > K<sup>+</sup>. The concentrations of dissolved silicate are heterogeneous, varying between 5.54 and 13.25 mg/l. The average value is  $8.88 \pm 2.70$  mg/l. The second group groundwater show relatively low total dissolved solids (TDS) contents, with values ranging from 857 to 898 mg l<sup>-1</sup>, the average value being  $613.30 \pm$  mg/l.

**Water-rock interaction processes:-**

Interactions between groundwater and surrounding host rocks are believed to be the main processes responsible for the observed chemical characteristics of groundwater in the study area. Evaluation of such processes requires the description of the main mineral assemblage of the rocks in which water is found, and the identification of chemical reactions responsible for the geochemical evolution of groundwater (Geroui et al, 2014, Rouabhia et al. 2010; Appelo and Postma,2005). From available studies in the literature, such reactions generally include chemical weathering of rock-forming minerals, dissolution-precipitation of secondary carbonates and ion exchange between water and clay minerals. In the present study, saturation indices (SI) with respect to carbonate (calcite, and dolomite), evaporate ( anhydrite and gypsum ), and siliceous (chalcedony ,quartz and amorphous silica), and minerals, as well as activities of soluble species, were calculated using the computer geochemical program PHREEQC and equilibrium partial pressure of CO<sub>2</sub>. Saturation indices (SI) are listed in (Table 3), for anhydrite (CaSO<sub>4</sub>), gypsum (CaSO<sub>4</sub>, 2H<sub>2</sub>O), calcite (CaCO<sub>3</sub>), dolomite (Ca, Mg (CO<sub>3</sub>)<sub>2</sub>), chalcedony, quartz and amorphous silica and were calculated for 10 samples.

The saturation indices for anhydrite and gypsum is below zero in all samples, which means that water is under saturated with respect to anhydrite and gypsum. Saturation index for calcite ranges between -0.25 and 0.23. 30% of the sample have SI >0, which means that they are oversaturated for precipitation of calcite and 30% of the samples have SI < 0 which means that they are under saturated with respect to calcite. For dolomite, Saturation index ranges between -2.2 and 1.9, and 51% of the samples have SI > 0, which means that they are oversaturated and precipitation of dolomite occurs. About 11% of the samples have SI = 0, which means equilibrium conditions and 38% of the samples have SI < 0, which means that they are undersaturated with respect to dolomite. All of the considered groundwater are saturated with respect to quartz and unsaturated with respect to chalcedony and to amorphous silica (table). The concentrations of dissolved SiO<sub>2</sub> in water samples may thus be influenced by these siliceous. All the Group A groundwater are under saturated with respect to calcite and dolomite (Fig. 5), suggesting that these carbonate mineral phases are absent in the corresponding host rock. In contrast, all the Group B groundwater are saturated with respect to calcite and dolomite indicating that these carbonate mineral phases may have influenced the chemical composition of this group of groundwater.

The distribution of the computed pCO<sub>2</sub> values for all the measured groundwaters is illustrated in table 3. For the studied period (May 2016), the calculated values appear to be considerably higher than atmospheric pressure (10<sup>-3.5</sup>) with values oscillating between 11.96 10<sup>-3</sup> to 1.90 10<sup>-3</sup>atm. The elevated values can be explained that the aquifers system is opened to the soil CO<sub>2</sub>.

**Table 3:- Saturation indexes and equilibrium partial pCO<sub>2</sub> of water springs**

ID	Anhydrite	Calcite	Dolomite	Gypsum	Chalcedony	Quartz	SiO <sub>2</sub> (a)	Siderite	pCO <sub>2</sub> 10 <sup>-3</sup> atm
S1	-2,03	-0.23	-0.86	-1.79	-0.03	0.41	-0.9	1.02	2.17
S2	-2,1	-0.25	-0.83	-1.86	-0.12	0.33	-0.98	0.80	2.32
S3	-2,06	0.16	0.22	-1,83	-0.37	0.07	-0,07	0.69	9.56
S4	-2,04	0.14	0.20	-1.81	-0.43	0,01	-1.29	0.46	11.96
S5	-2.21	-0.19	-0.73	-1.97	-0.21	0.24	-1.07	0.73	2.52
S6	-2.4	-0.13	-0.44	-2.16	-0.19	0.25	-1,05	0.61	1.94
S7	-2,42	-0.16	-0.7	-2.18	-0.08	0,37	-0.94	0.46	1.89
S8	-2.25	-0.17	-0.70	-2.02	-0.32	0.13	-1.17	0.80	2.28
S9	-2.31	-0.06	-0,49	-2.08	-0.43	0.01	-1.28	0.86	1.90
S10	-2.45	0.23	0.31	-2.21	-0.80	0.26	-1.04	0.89	7.62

**Drinking water quality:-**

The purpose of this section is to characterize the waters for both drinking as well as for irrigation purposes. Water was classified in Table 3 based on total hardness according to the classification of Sawyer and McCarty (1967).

Hardness is indicated from the presence of divalent metallic cations of which calcium and magnesium are the most abundant in groundwater. These ions react with soap to form precipitates. Hard water is unsatisfactory for household cleaning purposes, hence, water-softening processes for removal of hardness are needed (Todd 1980). Total hardness is calculated through the following formula:

$$TH = 2.497 \text{ Ca}^{2+} (\text{mg/l}) + 4.115 \text{ Mg}^{2+} (\text{mg/l})$$

It was observed that the examined water samples collected from springs were found to be hard, except the M2 which is located in the eastern part of the area studied. This water sample is classified as very hard water.

The calcium concentration is about  $67.20 \pm 12.540$  mg/l. It is apparent that S4 showed higher calcium content compared to the other stations. WHO guidelines, 2011 did not specify a permissible limit for calcium in drinking water, but stated that calcium permissible limit in groundwater should be 75 mg/l. according to the WHO (2011) guidelines; groundwater samples in the study area are acceptable for drinking purposes Except for S3 and S4 with 87 and 90mg/l respectively. Magnesium Concentration is  $21.26 \pm 9.56$  mg/l. It is evident that the water samples had a magnesium concentration within the permissible limit of 100 mg/l. Sodium can be tasted at concentrations of 200 mg/l or more as stated in WHO guidelines for drinking water (WHO, 2011). When exceeding the limit, it gives salty taste together with the presence of chloride. The mean sodium concentration is  $114 \pm 44.03$  mg/l. It is apparent that the water of the Mahouna massif showed generally sodium values within the permissible limit of 200 mg/l. The mean potassium concentration is  $2.99 \pm 1.63$  water indicates a low concentration of potassium (max= 6mg/l) compared to the permissible limit of 10 mg/l (WHO, 2011). The mean ferrous iron ( $Fe^{2+}$ ) value is  $2.99 \pm 1.47$  mg/l, ferrous iron concentration is over the permissible limit of 1.0 mg/l (WHO,2011); groundwater samples in the study area are not acceptable for drinking purposes.

#### Variation of anions:-

The mean bicarbonate value is  $191 \pm 65.08$  mg/l. Although, there are no exact permissible limits for bicarbonate in WHO guidelines (2011), the presence of  $HCO_3^-$  in drinking water should not exceed 500 mg/l in order to be safe for human consumption.  $HCO_3^-$  has a critical contribution to alkalinity of groundwater (Mohsin et al., 2013). The average chloride concentration in the Study area is  $191 \pm 65.08$  mg/l (station 6). High chloride values are recorded in the spring (S7) compared to the other stations where chloride values are below the permissible limit of 250 mg/l. The mean sulfate concentration is  $49.65 \pm 14.87$  mg/l showing sulfate values or all springs under the permissible limit of 250 mg/l. Nitrates in drinking water are a major contaminant in Algeria (Rouabhia et al. 2008; Fehdi, 2014). They are nowadays frequently found in aquifers. Nitrate ( $NO_3^-$ ) concentrations of the waters samples (Table 1) were found far under the World Health Organization (WHO 2011) recommended limit (50 mg l<sup>-1</sup>) especially for those samples occurring in Mountain areas. The mean nitrate concentration is  $10.54 \pm 7.60$  mg/l. The waters samples showed nitrate values under the permissible limit of 50 mg/l (table1). The high concentration of nitrates in water samples are the result agricultural activity in the area.

#### Suitability for irrigation:-

In order to assess the groundwater for irrigation practices, it should be analyzed using number of criteria. Water samples will be evaluated through four different methods. Soluble sodium percent (SSP), Sodium adsorption ratio (SAR) and Residual carbonate Sodium (RSC).

#### Soluble sodium percent (SSP):-

Soils containing a large proportion of sodium with carbonate as the predominant anion are termed alkali soils; those with chloride or sulfate as the predominant anion are saline soils, ordinarily, either type of sodium enriched soil will support little or no plant growth (Todd, 1980). Sodium content is usually expressed in terms of percent sodium defined by the equation:

$$Na^+ (\%) = 100. [(Na^+ / (Na^+ + Ca^{2+} + Mg^{2+}))]$$

Values relating to sodium percentage( table4), shows that most of the groundwater samples (80%) fall in the category of excellent and 20% to Doubtful to unsuitable for irrigation purposes.

#### Sodium Absorption Ratio (SAR):-

Sodium is one of the most studied cations, because of its toxicity effects on crops and well-known effects on soil texture. High concentration of sodium disperses soil colloidal particles, causing the soil to be hard and resistant to water diffusion. The osmotic pressure in the soil then builds up and causes complications in water to be absorbed by plant roots (Richards, 1954). SAR is expressed as the formula (US Salinity Laboratory, 1954), where values of  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  are in meq/l.

$$SAR = Na^+ / \sqrt{Ca^{2+} + Mg^{2+} / 2}$$

The SAR value varies from 0.66 to 4.54 with an average of 2.87. All Samples are suitable for irrigation (Table 4)

#### Residual Sodium Carbonate (RSC):-

The high concentration of bicarbonate ions in water provokes the precipitation of  $Ca^{2+}$  and  $Mg^{2+}$  as carbonates and

then the proportion of sodium in the soil increases. The RSC is calculated using the following equation:

$$\text{RSC} = (\text{HCO}_3^- \times 0,0333) (\text{Ca}^{2+} + \text{Mg}^{2+})$$

The concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are in meq/l and alkalinity values in mg/l.

Irrigation water having RSC values greater than 5 meq/l, have been considered harmful to the growth of plants, while waters with RSC values above 2.5 meq/l are unsuitable for irrigation. An RSC value between 1.25 and 2.5 meq/l is considered as the marginal quality and value < 1.25 meq/l as the safe limit for irrigation (Richards 1954). The calculated RSC values in the groundwater samples of Bouchegouf aquifer are found to vary from -3,85 to 1.14 meq/l with an average of -1.38 meq/l (Table 4). Regarding to the RSC values, all samples are suitable for agricultural purposes.

**Table 4.** -Results of the calculations of SAR, SSP and RSC

ID	SAR	SSP (%)	RSC
S1	4.54	54.08	8.17
S2	3.59	51.68	7.77
S3	1.42	31.40	13.06
S4	1.28	24.53	16.51
S5	3.98	56.24	7.91
S6	1.07	56.48	8.19
S7	4.07	66.57	6.98
S8	3.61	56.57	7.13
S9	4.53	62.89	7.41
S10	0.66	8.70	14.44
Mean	2.87	46.88	9.57

### Conclusion:-

This study has thrown light on hydrochemical quality of springs in Mahouna Massif, as well as on the status of the water quality in the study area. Physicochemical parameters showed that the waters springs are suited for drinking and domestic uses due to low amounts of cations and anions, except for calcium which present an amount over the permissible limit of WHO. According to SAR, SSP and RSC water samples are suitable for irrigation uses.

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