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RESEARCH ARTICLE

HYDROCHEMISTRY OF WATER SPRINGS OF THE TRAVERTINE AQUIFER OF GUELMA IN NORTH-EAST OF ALGERIA.

*Nouar T., Geroui Y. and Toumi A.

Civil Engineering and Hydraulic Laboratory, PO Box 401, University 8 mai 1945, Guelma, 24000. Algeria.

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Abstract

This work was conducted on ten water springs of the travertine aquifer of Guelma in north-east of Algeria. The physical parameters (pH), Electric Conductivity (EC), Total Dissolved Solids (TDS), TH as well as the concentrations in major ions Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- , NO_3^- and SiO_2 analyzed by standard methods. Hydrochemical facies predominant in the study area is Ca-Mg- 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 aquifer are within the limits allowed for the drinking water according to WHO guidelines purposes. Soluble sodium percent, SAR, RSC and Magnesium hazard reveal that, barring a few locations, most of the groundwater samples are safe for irrigation purposes.

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Introduction:-

In Algeria and in Guelma in particular, the supply of water for different purposes depended largely on groundwater, where the surface waters are heavily polluted. Economic development, agriculture and population growth result in an increased need exceeding the potentialities of the alluvial aquifer, which requires capturing springs which emerge from the travertine aquifer. Ultimately, to satisfy the suburban area in water for human consumption and water demand for crops irrigation. The main objectives of this study are physicochemical parameters, the identification of chemical processes that are responsible of groundwater chemistry and suitability for drinking water and irrigation purposes of the waters springs of the travertine aquifer.

Material and Methods:-

Seven major waters springs (Table 1) were sampled in May 2016 for the purpose of this investigation. The geographical location of the sampling sites is shown in Figure 1. Field measurements of TDS, pH and alkalinity were determined at all sampling sites. Alkalinity was determined using colorimetric titration with sulphuric acid (0.1N). Other chemical analyses (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , NO_3^- and dissolved silica) and isotopic analyses were carried out later in the laboratory. Calcium, Mg^{2+} , Na^+ , K^+ and aqueous silica concentrations were determined by flame photospectrometry. Concentrations of Chloride, Nitrates and sulfates were determined using ion chromatography at the Civil Engineering and Hydraulic Laboratory at Guelma University. The hydrochemical calculations were performed using the Diagram program (Simler, 2003), which makes it possible using PHREEQC

Corresponding Author:- Nouar T.

Address: Civil Engineering and Hydraulic Laboratory, PO Box 401, University 8 mai 1945, Guelma, 24000. Algeria.

(Parkhurst and Appelo, 1999). The computer processing of these hydrochemical data had a main objective: the determination of the saturation indexes of minerals such, Aragonite, calcite, dolomite, chalcedony, quartz, amorphous silica and gypsum, and the partial equilibrium pressure of CO₂.

Study Area:-

The study area is located in Guelma district in the extreme North East of Algeria with a surface of about 13 km². The travertine aquifer constitutes an important water resource not exploited by boreholes. Many springs emerge in this locality and its water contributes in drinking purposes and irrigation of the south part of Guelma. The study area is characterized by an elevation of about 250 to 575 m above the sea (msl). The outcrops are occupied by the mastic and olives trees in South, and cereals; fruit trees and vegetables in North. In the center, they are occupied by urban zone extension of Guelma City(Figure1).The climate of the study area is considered to be semi tempered, the annual average precipitation being approximately 555mm. Rainfall occurs from august to June, with a maximum during January and February of each year. The average temperature is approximately 12°C in winter and 26°C in summer, though summer high temperature can reach 40°C in July. Annual total evaporation rises to 886.71 mm. The geology of the area was studied by several authors (Vila, 1980; Chouabbi 1987).It consists by travertine rich with aragonite, calcite and siliceous jasper bedded on Pliocene clay basement. The aquifer is mainly recharged by precipitation, secondarily by the contacts with the Numidian sandstones in South of the study area (Benmarce, 2007).

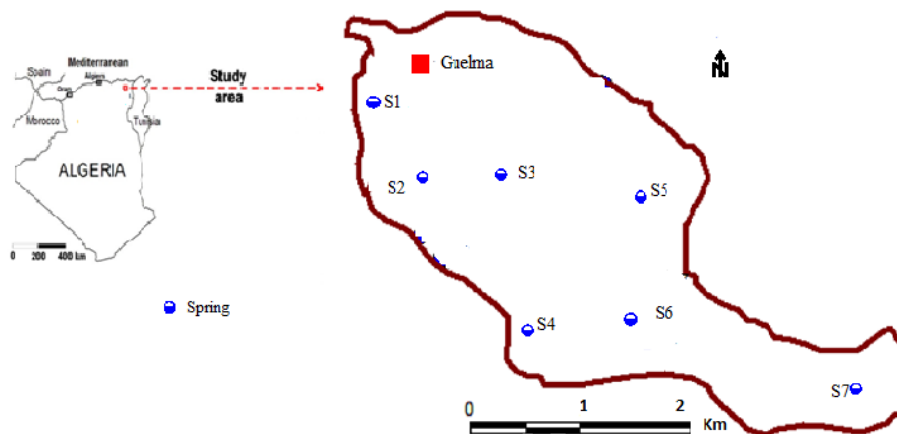


Fig 1:- Location of the study area in eastern part of Algeria

Results and Discussion:

Chemical Characteristics:

Physical and Chemical data, minimum, maximum, mean and Standard deviation of all the springs water are summarized in Tables 1 and 2. Among the major cations (Table 1), a predominance of Ca²⁺ and Na⁺ is observed for this groundwater samples. Concentrations of both Ca²⁺ and Na⁺ (in mg l⁻¹) represent on average 67.27 and 26.15% of all the cations, respectively. Mg²⁺ and K⁺ ions are secondary in importance, representing on average 11.58 % of all cations. Among the major anions (table 1), HCO₃⁻ is also dominated, representing on average 73.69 % of all the anions. The Cl⁻, SO₄²⁻ and NO₃⁻ ions are less abundant; they represent on average 15.80, 8.29 and 2.19% of all the anions, respectively. The concentrations of dissolved silica are heterogeneous, varying between 5.70 and 13 mg/l.

Table 1:- Chemical composition (in mg/L) of groundwater from Travertine aquifer.

ID	TDS	pH	EC	TH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	SiO ₂
S1	550	7.53	683	316.50	110	10	42	1.72	269	63	22	4.30	8.20
S2	548	7.56	704	278.50	95	12	53	2.50	256	65	48	6.23	6.23
S3	592	7.50	752	322	102	16.16	52	2.22	298	78	24.6	5.70	5.70
S4	585	7.60	708	300.50	87	20	48	3.00	320	56	22	9.25	9.25
S5	498	7.58	624	292.50	90	18	24	5.5	213	55	52	7.53	7.53
S6	491	7.50	618	279	85	16	39	2.50	235	52	22	12	12
S7	525	7.54	603	295.50	100	11	23	4.00	288	34	21	11.02	13

TDS total dissolved solids (mg/l), EC electrical conductivity (μS/cm and pH unit pH

Table 2:- Descriptive Statistics of hydro chemical data of water springs

Statistic	TDS	pH	EC	TH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	SiO ₂
Min	491	7.50	603	279.50	85	10	23	1.72	213	34	21	4.23	5.70
Max	592	7.60	752	322	110	20	53	5.15	320	78	52	12.00	13
Mean	541.29	7.54	670.29	297.50	95.57	14.4	40.14	3.01	268.43	57.57	30.23	7.99	8.84
SD	39.31	0.04	55.98	16.87	9.00	3.78	12.43	1.18	37.11	13.53	13.60	2.87	2.78

Mechanisms influencing the chemistry and water-rock interaction Processes:-

The ratio of $Na^+ + K^+ / (Na^+ + Ca^{2+})$ and $Cl^- / (Cl^- + HCO_3^-)$ as a function of TDS are widely employed to determine the processes of dissolved chemical constituents, such as precipitation, rock and evaporation dominance (Gibbs 1970,1971). According to the Gibbs classification the groundwater water samples of the study area indicate that evaporation dominance mechanisms control the chemistry of the groundwaters of the area. (Figure 2a and b). Another factor may be involved in the control of water chemistry such as dissolution and precipitation of rocks minerals in the study area .Mineral equilibrium calculations for groundwater are useful in predicting the presence of reactive minerals in the groundwater system and estimating mineral reactivity. By using the saturation index (SI) approach, it is possible to predict the reactive mineralogy of the subsurface from groundwater data without collecting the samples of the solid phase and analyzing the mineralogy (Deutsch 1997, Rouabhia et al, 2012). In the present study, equilibrium partial pressure of CO₂, saturation indices (SI) with respect to carbonate (aragonite, calcite and dolomite) and to siliceous (quartz, chalcedony and amorphous silica) minerals were calculated based on the following equation (Lloyd and Heathcoat 1985):

$$SI = \log (IAP / K_s (T))$$

Where IAP is the ion activity product of the solution, and K_s (T) is the equilibrium constant of the reaction considered at the temperature T.

The computed values of SI and pCO₂ for all minerals are summarized in (Table 3). For the stage period, the calculated values appear to be considerably higher than atmospheric pressure (10^{-3.5}) with values varying between to 1.10 10⁻² to 0.60 10⁻²atm. The elevated values can be explained that the travertine aquifer is opened to the soil CO₂. All the considered ground waters are in oversaturated with respect to aragonite, calcite and to dolomite (SI>0), which means that they are oversaturated for precipitation of aragonite, calcite and dolomite, suggesting that these carbonate mineral phases are present in the study area and carbonate mineral phases may have influenced the chemical composition of this ground waters. Generally, groundwater are saturated with respect to quartz (SI>0) and under saturated (SI<) with respect to chalcedony and under saturated with respect to amorphous silica, and these siliceous minerals can influence the concentrations of the dissolved SiO₂ in groundwater.

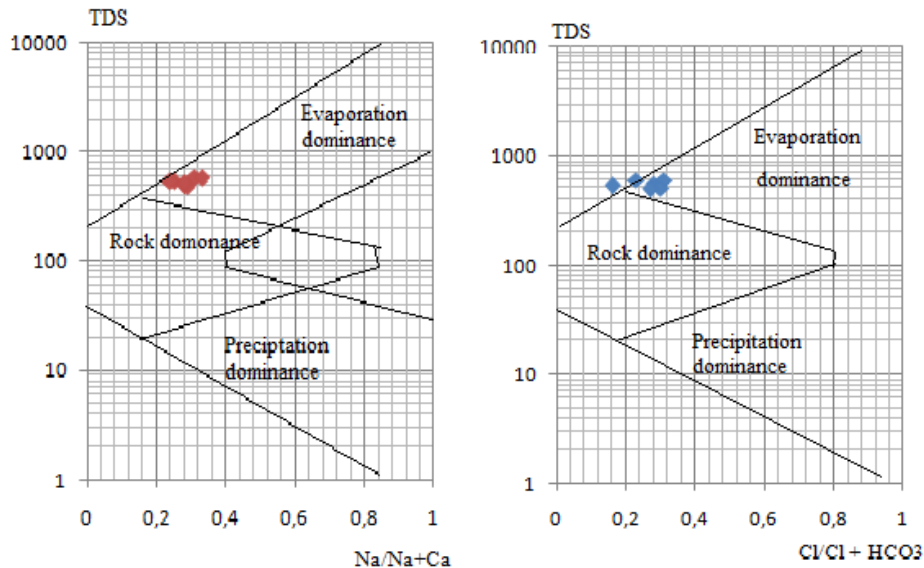


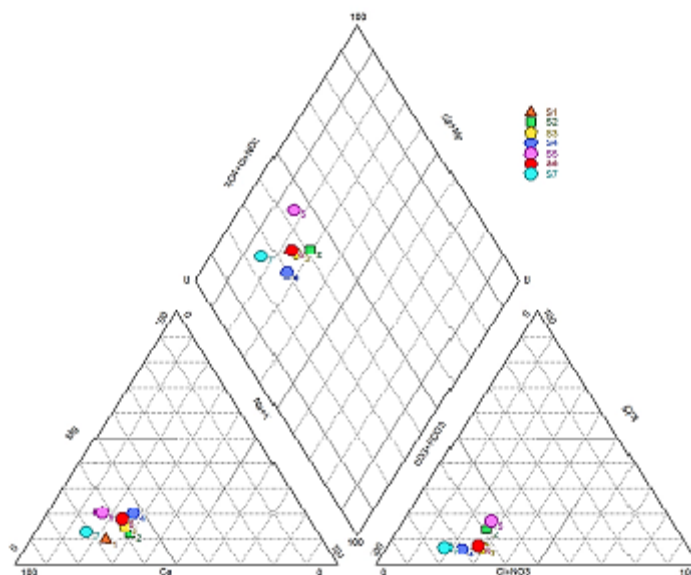
Fig 2:- Plot of some groundwater samples in the Gibbs diagram (a: TDS vsNa/Na+Ca ; b: TDSvs Cl/Cl+HCO3)

Table 3:- Saturation indexes and equilibrium partial pCO₂ as computed with PHREEQC.

ID	Aragonite	Calcite	Dolomite	Chalcedony	Quartz	SiO ₂	pCO ₂ 10 ⁻² atm
S1	0.50	0.50	0.31	-0.31	0.11	-1.15	0.85
S2	0.30	0.44	0.33	-0.43	0.00	-1.27	0.76
S3	0.33	0.48	0.50	-0.47	-0.04	-1.31	1.10
S4	0.40	0.54	0.80	-0.26	0.17	-1.10	0.86
S5	0.22	0.37	0.58	-0.35	0.08	-1.19	0.60
S6	0.22	0.32	0.26	-0.15	0.28	-0.91	0.80
S7	0.37	0.51	0.41	-0.11	0.31	-0.95	0.89

Hydrochemical Facies:

The chemical data obtained from waters springs samples are plotted on a Piper trilinear diagram (1944) to understand the hydrogeochemical regime in the study area during the stage period. The piper diagram (Fig. 5) constructed using Diagram Scientific Software shows the relative concentrations of the different ions of analyzed water samples. One main hydro chemical facies (Ca-HCO₃) type, were identified based on the concentrations of the major ions, which indicates the dominance of carbonate rocks in the area.

**Fig 3:-** Trilinear Piper diagram**Drinking Water Purposes:-****Physical Parameters:-**

From the table1, the pH from springs water of the travertine aquifer is found to be ranging from a minimum of 7.50 to a maximum of 7.60 with a mean of 7.54. These values show that the waters are moderate to slightly alkaline. All samples were found to below than the permissible limit of (6.5 to 8.5) prescribed by WHO (2011) for drinking water. Total Dissolved Solids (TDS) are the total amount of mobile charged ions, including minerals, salts or metals dissolved in a given volume of water. Total dissolved solids (TDS) varied from 491 to 592 mg/l with a mean value of 541.29 mg/l. As per TDS classification, 100% of the springs are fresh (TDS <1,000) water type (Freeze and Cherry, 1979). Electrical conductivity is the numerical expression of the ability of a water sample to carry an electric current and could be a sign of productivity of the water body. Results from this study showed that values of conductivity are ranging between 603 to 752 μS/cm with an average of 670.29 μS /cm. According to WHO guidelines, waters of the study area show a slightly mineralization and EC values are between the minimum desirable and maximum permissible by WHO (500- 1400 μs/cm). Saxena et al., (2003); and Prakash and Somashekar (2006) regrouped waters into three classes, fresh water if the EC <1500 μS / cm, brackish water if the EC is between 1500 -3000 μS/cm, and salt water if the EC > 3000 μS/cm. According to this classification, all samples waters of the springs are freshwater and were used to the drinking and domestic purposes.

In groundwater, hardness is formed mainly due to carbonate, bicarbonate and chloride of Ca^{2+} and Mg^{2+} . As a water quality parameter, TH values can be used to classify water for domestic, agriculture and industrial uses. Total hardness (TH) ranges from 400.50 to 650 mg/l with an average value of 557.70 ± 88.66 mg/l. According to WHO standards, the most desirable limit is 300 mg/l and the maximum allowable limit of TH for drinking is 600 mg/l. The classification of groundwater based on TH shows that a majority of the groundwater samples of the study area falls in the hard to very hard water category (WHO, 2011). Hence, classification of the groundwater of the study area based on total hardness (Sawyer and McCarthy, 1967) has been carried out and is presented in Table 3. Based on TH in the study area all samples fall under very hard class. According to WHO guidelines (2011) and Sawyer and McCarthy (1967), waters of springs are suitable for drinking and domestic purposes.

Major Cations and Anions:-

The concentration of Ca^{2+} in the study area ranges from 85 to 110 mg/l with an average of 95.57 mg/l. 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 considered not acceptable for drinking purpose.

The major source of Ca^{2+} in the groundwater is due to dissolution carbonate minerals from rocks of this area. Mg^{2+} contents is low in the water samples of the study area, ranges from 10 to 20 mg/l with a mean value of 14.40 mg/l. we can be observed from the tables (Table1) that magnesium concentration from water samples is very low and safe for drinking and domestic uses. Sodium (Na^+) contents in waters springs ranges from 23 to 53 mg/l with a mean value of 40.14 mg/l. According to WHO (2011) standards, the maximum admissible limit is 200 mg/l. Waters samples of springs show concentration of Na^+ below the permissible limit (WHO2011). Potassium (K^+) concentration ranges from 1.72 to 5.15 mg/l with an average value of 3.01 mg/l. The majority of samples are below 2 mg/l and there is no threat from potassium in waters samples.

HCO_3^- is easily dissolve in water and usually originates from weathering of feldspars and ferro-magnesium minerals by carbonic acid (Monjerezi et al., 2012). HCO_3^- is easily dissolve in water and usually originates from weathering of feldspars and ferro-magnesium minerals by carbonic acid (Monjerezi et al., 2012). As well, it comes from dissolution of carbonate rocks and water-rock interaction (Murad et al., 2011). The bicarbonates (HCO_3^-) is the dominant anion and the contents vary from 213 to 320 mg/l with a mean of 268.42 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 (Table1). A concentration of chlorides (Cl^-) in water springs oscillates from 34 to 78 mg/l with a mean value of 57.57 mg/l. The desirable limit of Chloride for drinking water is specified as 250 mg/l as per WHO (2011) and all the samples are under this limit. The concentration of sulfates (SO_4^{2-}) varies from 21 to 52 mg/l with a mean value of 30.60 mg/l, and 100% of water sample are within allowed limit and can be used for human consumption.

Nitrates (NO_3^-) concentration from springs, ranges from 4.23 to 12 mg/l an average of 7.99 mg/l. 100% of the samples are within the permissible limit of 50 mg/l (WHO,2011). Relatively higher concentrations were observed in samples from the S6 and S7 located near the agricultural areas, where potential sources of nitrate contamination are more prevalent. Concentrations between 0 to 40 mg/l are generally safe for human adults and livestock; and do not use for human infants (Khanfar, 2010).

Suitability for Irrigation:-

Sodium Adsorption Ratio:-

Water is excellent for irrigation purposes if the SAR is under 10 (Richards,1954). The SAR values are calculated according to the following formula:

$$\text{SAR} = \text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+})^{1/2}$$

The concentration $\text{Ca}^{2+} + \text{Mg}^{2+}$ and Na^+ are in meq/l

There is a significant relationship between SAR values of irrigation water and the extent to which sodium is absorbed by the soils. If water used for irrigation is high in sodium and low in calcium, the cation exchange complex may become saturated with sodium. This can destroy the soil structure owing to dispersion of the clay particles. Water having $\text{SAR} < 10$ are excellent and suitable for all types of crops and all types of soils, except for those crops,

which are sensitive to sodium. The calculated SAR values in the groundwater samples of travertine aquifer are found to vary from 0.68 to 1.42 with a mean of 1.25 (Table 4).

Residual Sodium Carbonate:-

The high concentration of bicarbonate ions in water provokes the precipitation of calcium and magnesium as carbonates and then the proportion of sodium in the soil increases. The RSC is calculated using the following equation:

$$\text{RSC} = (\text{Alkalinity} \times 0.0333) (\text{Ca}^{2+} + \text{Mg}^{2+})$$

The concentration of alkalinity values in mg/l and $\text{Ca}^{2+} + \text{Mg}^{2+}$ are in meq/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 >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 estimated RSC values in the groundwater samples of travertine aquifer are found to vary from 1.24 to 4.64 meq/l with a mean of 2.89 (Table 4). According to RSC values; 86% samples are unsuitable for irrigation (Richards, 1954).

Percent Soluble Sodium (SSP):

$$\text{SSP} = [\text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+)] \times 100$$

Where, Ca^{2+} , Mg^{2+} and Na^+ are concentrations in meq/l.

SSP values less or equal to 50 indicate good quality water while values greater than 50 are contrary and unsuitable for irrigation (Wilcox, 1955). SSP values ranged between with a mean of 16.52 to 29.53% with a mean of 24.23% (Table 4). The soluble percent sodium concentration in all samples belongs to the excellent to good categories and is used to agricultural purposes.

Magnesium Ratio:-

A ratio namely index of magnesium hazard was developed by Paliwal (1972) and was calculated by the following equation:

Where, all the ions are expressed in meq/l.

$$\text{Mg}^{2+} \text{ Ratio} = 100 \times [(\text{Mg}^{2+} / \text{Ca}^{2+} + \text{Mg}^{2+})]$$

Magnesium hazard oscillated between 13.11 and 27.72% with a mean value of 20.55%. 100% of samples fall below the permissible limit of 50% indicating the favorable effect on crop yield and decrease in soil alkalinity (Table 4). In the study area all of the samples are suitable for agricultural purposes regarding Magnesium hazard.

Table 4:- Results of the calculations of SAR, SSP, RSC, and Mg hazard

ID	SAR	SSP (%)	RSC	Mg (%)
S1	0.78	23.07	2.62	13.11
S2	1.42	29.53	2.77	17.39
S3	1.31	26.73	3.07	20.80
S4	1.27	26.88	4.64	27.72
S5	0.97	22.51	1.24	25.64
S6	1.07	24.39	2.24	23.83
S7	0.68	16.52	3.68	15.39
Mean	1.25	24.23	2.89	20.55

Conclusions:-

In the study area, the waters springs of the travertine aquifer of Guelma was important water resources in this area. It is the main water resource used for drinking and agricultural purposes. Therefore, determining the source and mechanism controlling the water chemistry is outlined in this study. Hence, analysis of the major ions in groundwater was carried out. The principal factor responsible of the chemical composition of the water is evaporation dominance, dissolution and precipitation of some minerals. Physicochemical analysis showed that the waters springs are suited for drinking and domestic uses due to low amounts of cations and anions, except for

calcium with preset an amount over the permissible limit of WHO. According to SAR, SSP, RSC and Mg hazard, ground water is suitable for irrigation uses.

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