Hydrochemistry and Assessment on Groundwater Quality of the Aquifer of Heliopolis in North of Guelma-Algeria

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Abstract: Groundwater quality assessment is important to ensure sustainable safe use of water. In the study area, the mountain aquifer represents the main source of water supply for drinking and agriculture seeing the shortage in superficial water in this area. In the present work, the first attempt has been made, for the first time in this region, to study the hydrochemistry and assessment on groundwater quality of the aquifer, based on an analysis of physical–chemical parameters to this purpose, water samples were collected during the period of may 2015 from 8 drills and 4springs to represent this ain aquifer. Methodology applied in this study is based on standard procedure. The water samples were investigated with respect to TDS, pH, CE; calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), chloride (Cl^{-}), sulphate (SO_4^{2-}), bicarbonates (HCO^{-}_3) and nitrate (NO^{-}_3). The analytical results obtained were interpreted using hydro chemical analysis. The results show that the waters have pH values ranging between 6.90 and 7.82, EC between 610 and 854 mg/L, TDS ranging between 455 and 672 mg/l and nitrate concentrations between 2.5 and 47.7 mg/L. The concentration of nitrates is explained by the utilization of chemical fertilizers in agriculture. All samples are of Ca-Mg–HCO_3 and Ca-Cl_2 and Ca-SO_4 water types. Physical and chemical analyses show that the most of the samples are fit for human consumption. Based on the analytical results, chemical indices like sodium adsorption ratio Kelly's index, Magnesium hazard and residual sodium carbonate were calculated which show that most of the samples are good for irrigation.

Keywords: Hydrochemistry, Groundwater, Assessment, Quality, Heliopolis, Algeria

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1. Introduction

Groundwater plays a dominant role in the Eastern part of Algeria. Because of the lack of permanent surface water reservoirs owing the quality of rivers is deteriorated by various forms of pollution. Water resources have become increasingly limited, difficult to exploit, and often are exposed to significant amounts of wastewater [1]; groundwater constitutes the most widely available source of fresh water. In this region, groundwater is used for domestic, agricultural and industrial purposes. Comprehensive hydro chemical studies of this groundwater have been carried out in civil Engineering and Hydraulic Laboratory, Guelma University. Results presented here are for groundwater from the Heliopolis aquifers (Figure. 1).

The study area is located 4 km north of the city of Guelma, which belongs to the eastern region Constantine plain [Gaud]. It lies between, 7°26'34"E - 36°30'13"N (Figure.1). The region is bounded by Djebel Beni Ahmed to the north and the Seybouse River to the south, by the hills of Bouzitoune and Djebel Debar to the west. The climate of the study area is considered to be tempered, the annual average precipitation being approximately 629.37 mm. The mean monthly temperatures are high, varying between 9, 65°C in January and 40°C in July, the mean annual value being 18.3°C. The mean annual potential evapotranspiration, according to the C.W Thornthwaite formula, is approximately 853.8 mm.

Geologically, the area constitutes a sub basin of collapse full of plio-quaternary alluvium deposits. All over the Seybouse watershed (Figure.2), the plio-quaternary is made of alluvia deposits with interspersions of gypsiferous formations. The structural domain is characterized by neritic socer constitutes the majority of the area and it characterized by an alternation of limestone and marl (Figure.2). Hydrogeological data of some boreholes dug in the area [3]. Mihoub (2016) suggests the presence of two aquifers. An alluvial aquifer has a thickness of 15 m, at a depth of 5 m and a neritic carbonate aquifer at a depth of 50 m to 350 m. These aquifers play an important role in drinking water supply for the local population and nearby agglomerations. A pumping test indicates a transmissivity of 10^{-3} m^2/s in this aquifer. The general direction of groundwater flow is from north to south [3]. The alluvial aquifer is mainly recharged by precipitation, fissured limestone and faults. The natural discharges of these aquifers are springs, boreholes and by evapotranspiration. This study aims to determine the hydrochemistry and assessment quality on groundwater in the Heliopolis area.

Figure 1. Location of the study area in Algerian Northeast

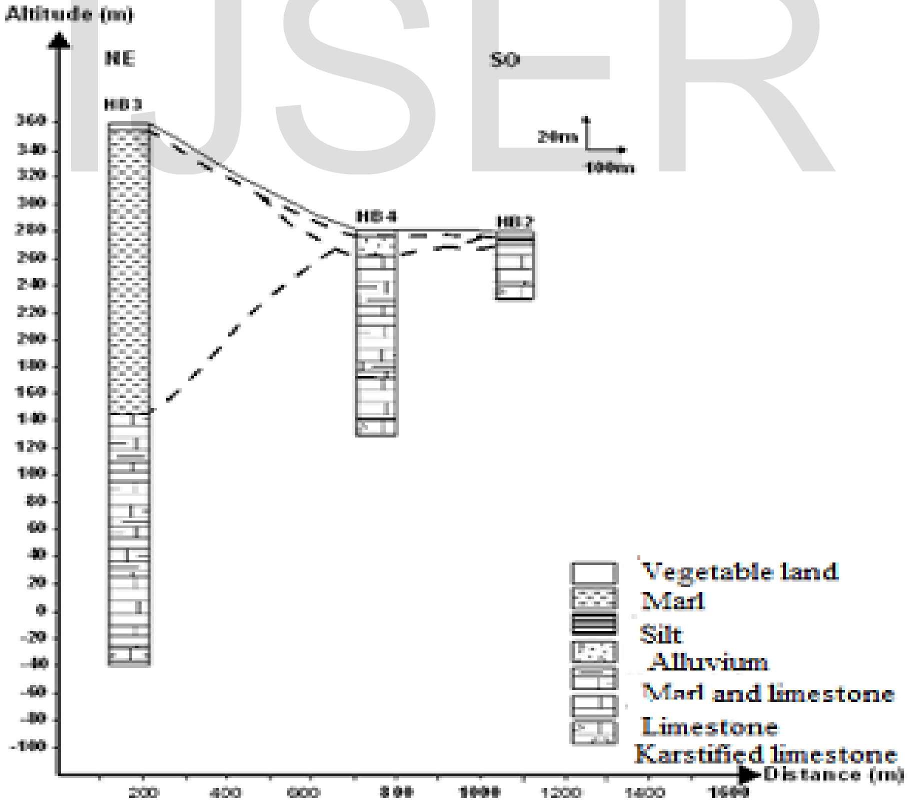

Figure 2.Hydrogeological cross-section through the Heliopolis plain

2. METHODOLOGY AND DATA

Methodology applied on this study is based on sampling by boreholes, springs and chemical analysis in the laboratory of Water chemistry at the University of Guelma. Eight boreholes ranging in depth from 15 to 50 m and four springs (Table 1) were sampled in August 2016 for the purpose of this investigation. The geographical location of the sampling sites is shown in Figure 1. Field measurements of pH and alkalinity were determined at all sampling sites. Alkalinity was determined using colorimetric titration with sulphuric acid. Other chemical analyses (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, CI^{-}, SO^{2-}_{4} and NO^{-}_{3}) were carried out later in the laboratory. Calcium, $Mg^{2+,}$ Na^{+}, K^{+} concentrations were determined by flame photospectrometry. Concentrations of Cl^{-}, $NO^{-}3$ and SO^{2-}_{4}were determined using ion chromatography. The results of hydrochemical analysis were compared to WHO standards [4]for the suitability evaluation of the samples water for drinking and domestic uses. To study the water quality for irrigation, sodium percent SAR), Magnesium ratio, Kelly's ratio and residual sodium carbonate (RSC) were calculated for agricultural purposes.

3. RESULTS AND DISCUSSION

The minimum, maximum, mean and standard deviation for each parameter is summarized in Tables1.

Table 1. Descriptive Statistics of the analyzed parameters in water samples of the Heliopolis aquifer

Variable	Minimum	Maximum	Mean	SD
TDS	455	672	552.83	66.60
pH	6.90	7.82	7.60	0.26
EC	610	854	729.33	76.53
Ca	63	110	86.16	14.10
Mg	14	36	21.66	5.63
Na	33	56.50	45.40	9.25
K	0	4	1.84	0.93
HCO3	200	345	243	41.58
Cl	56	100	76.8	12.97
SO4	34	200	65	45,91
NO3	4	36	14.16	9.39

3.1 Hydrochemical Facies and Mechanisms Controlling the Hydrochemistry

Piper's diagram (1944) is useful for displaying the results of analysis in a multi coordinate field. The results were plotted on a Piper's diagram. The geochemical evolution of groundwater can be understood by plotting the concentrations of major cations and anions in the Piper trilinear diagram [5]. The plot shows that some samples also represent, mixed Ca–Mg- HCO3-Ca- Cl_2 and Ca- SO4 types (Figure 3).

Plots of Gibbs ratios of groundwater samples on Gibbs diagrams [6] can provide information on the relative importance of three major natural mechanisms controlling water chemistry: atmospheric precipitation, mineral weathering, and evaporation and fractional crystallization. The Gibbs diagram shows that, groundwater samples plot either in rock dominance (Figure 4).

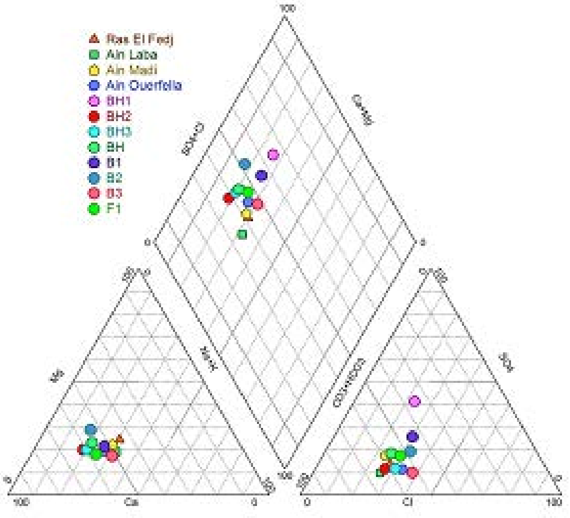

Figure 3. Piper diagram of the groundwater samples in the study area

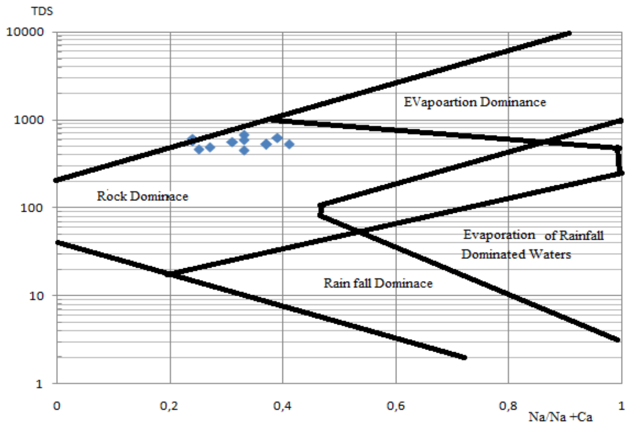

Figure 4. Gibbs plot indicating the mechanisms that determine the major ion composition of groundwater in Heliopolis aquifer

3.2 SATURATION INDEX

The saturation index (SI) is a widely used indicator in hydrogeochemical studies. The hydrochemical calculations were performed using the AQUACHEM program [7], which makes it possible using PHREEQC [8] was used to compute the saturation index (SI) of certain major minerals, including anhydrite, calcite, dolomite and gypsum. When SI = 0, the minerals in the aqueous solution are in equilibrium. When SI < 0, the minerals in the aqueous solution are unsaturated and follow a dissolution trend, and when SI > 0, the oversaturated status of minerals in the aqueous solution causes deposition to occur. Several authors can be considered SI as the principal process responsible for the chemical appearances of groundwater in [9, 10, 11]. The saturation index (SI) is defined as; dissolution trend, and when SI > 0, the supersaturated status of minerals in the aqueous solution causes deposition to occur. The saturation index (SI) is defined as:

$$SI=\log\ (IAP/K_T) \tag{2}$$

Where IAP is the relevant ion activity product in a mineral dissolution reaction, which can be obtained by multiplying the ion activity coefficient γi and composition concentration mi; and K is the equilibrium constant of mineral dissolution at a 25°C. The saturation indices for aragonite, calcite, dolomite and gypsum were calculated with PHREEQC [8]. The calculation results are listed in Table 2. The calculated values of SI for calcite, dolomite, and gypsum range from -1.12 to 0.64, 1.21 to 1.98, and -3.18 to -0.22 with averages 0.05, 0.21, and -1.63, respectively. About 70% of the groundwater samples were kinetically oversaturated with respect to calcite and dolomite, and all the samples were below the equilibrium state with gypsum.

The distribution of the calculated pCO2 values for all the measured groundwaters is illustrated in table 2. For the stage period, the calculated values appear to be considerably higher than atmospheric pressure ($10^{-3.5}$) with values varying between 0.31 and 3.39 10^{-2} atm. The elevated values can be explained that the e carbon mineralization occurs in open system.

Table 2.Saturation indexes and equilibrium partial pressure (pCO2) as computed with PHREEQC

ID	Aragonite	Calcite	Dolomite	Gypsum	pCO2 10^{-2}atm
Ain el Fedj	-0.55	- 0.40	-0.97	-1.97	3.39
Ain Laba	0.27	0.42	0.52	-1.99	1.04
Ain Madi	0.12	0.26	0.29	-1.84	0.74
Ain Ourfella	0.20	*-0,05*	-0.44	-2.08	1.09
BH1	0.38	0.51	0.51	-1.29	0.55
BH2	0.65	0.93	0.93	-1.87	0.63
BH3	0.47	0.58	0.58	-2.00	0.42
BH4	0.43	0.59	0.59	-1.80	0.43
B1	0.46	0.62	0.62	-1.56	0.36
B2	0.62	1.06	1.06	-1.63	0.38
B3	0.53	0.67	0.67	--2.02	0.31
F1	0.57	0.72	0.72	-1.73	0.39

3.3 SUITABILITY FOR DRINKING WATER

3.3.1 Physical Parameters

The pH of the groundwater is within the range of 6.90 to 7.82 with a mean of 7.60, indicating alkalescent tendency standards. The mineralization of water varied with electrical conductivity. The mean value of electrical conductivity was 729.33µS/cm. Total dissolved solids are measure of the amount of dissolved material in water. The presence of such solutes alters the physical and chemical properties of water. In the study area, The TDS in the groundwater ranges from 455 to 854 mg/L, indicating fresh to moderately mineralized water [4]. Water hardness is caused primarily by the presence of cations such as calcium and magnesium and anions such as carbonate, bicarbonate, chloride and sulphate in water. Total Hardness was computed by the following formula [12]:

$$TH = (Ca+ Mg) \times 50 \qquad (3)$$

In the study area, the total hardness varies between 241.50 to 402.26 mg/l and 308.43mg/l. According to Total Hardness classification [4] most of the groundwater samples in the study area are very hard (>180 mg/l as CaCO3).

3.3.2 Chemical Parameters

Among cations, calcium showed concentration between 63 to 110 mg/l with a mean of 86.16 mg/l. Abundance of calcium was imparted to limestones and calcareous crusts exposed in the study area. WHO guidelines (2011) did not specify a permissible limit for calcium in drinking water, but stated that calcium permissible limit in groundwater should be 75mg/l. according to the WHO guidelines; 83% of groundwater samples in the study area are considered not acceptable for drinking purposes. Magnesium concentration in the groundwater samples of the study area, varying from 14 to 36 mg/l with an average value of 21.16 mg/l. It can be observed from the tables (Table 1) that magnesium concentration in the groundwater samples is very low and suitable for domestic purpose. Mg^{2+} may probably have been derived from the same source as that of Ca^{2+}. Sodium concentration in groundwater samples ranges from 33 to 56.50mg/l with an average of 45.40 mg/l. According to WHO (2011) guidelines, the maximum admissible limit is 200 mg/l. Groundwater samples of all samples show concentration of Na+ lower than the permissible limit. Potassium concentrations are relatively low compared to the concentrations of other cations, with values varying between 0.90 and 4 mg/l. Potassium content in groundwater samples are vey lower and there is no threat from K^+ in groundwater [13].

Among anions, HCO3- ion concentration varied from 200 to 345 mg/ l with mean concentration of 235 mg/.HCO^-_3 is easily dissolve in water and usually originates from weathering of feldspars and ferro-magnesium minerals by carbonic acid [14]. As well, it comes from dissolution of carbonate rocks and water-rock interaction ([15]. Although, there are no exact permissible limits for bicarbonate in WHO guidelines, the presence of HCO3- 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 ([16], chloride ranges from 56 to 100 mg/l with mean concentration of 76.80 mg/l. Chloride usually forms different compositions of salts such as sodium chloride (NaCl), potassium chloride (KCl) and calcium chloride ($CaCl_2$). Concentration of Cl^- in the area is considered low comparing with WHO standards (250 mg/l). The concentration of sulphate ranges from 34 to 200 mg/l with mean concentration of 65 mg/l. Sulphate is derived from gypsum (CaSO4, 2H2O) and oxidation of sulphide minerals [17], more than 250 mg/l in water causes bitter taste, laxative effects for some people, and corrosion of water pipes and distributing systems. Sulphate ion concentration in the present study area is lower than the suggested standards by WHO (2011). Nitrates (NO^-_3) are the end product of aerobic stabilization of organic nitrogen and a product of conversion of nitrogenous material, and as such occur in polluted water. Nitrate content in drinking water is considered important for its adverse health effects. The occurrence of high levels of nitrate in groundwater is a prominent problem in many parts of Algeria. The nitrate concentration of groundwater samples range from 4 to 36 mg/l with an average value of 14.64 mg/l. The desirable limit of nitrate for drinking water is specified as 50 mg/l. With low concentration, nitrate has not health effect.

3.3.4 Suitability for Irrigation Purpose

Excessive concentrations of dissolved ions in the water used for irrigation affect plants and the physical and chemical parameters of soil by lowering the osmotic pressure in the plant structural cells [18].This process prevents water from reaching the branches and leaves, thus reducing the agricultural productivity. Percent sodium (Na^+), Residual sodium carbonate (RSC), and Magnesium hazard indices were computed for the assessment of the suitability of water quality for irrigation purpose in the study area.

Percent sodium.

Excess sodium in waters produces undesirable effects of changing soil properties and reducing soil permeability [20]. The sodium percentage (Na %) is calculated using the formula given below, where all the concentrations are expressed in milliequivalents per liter:

$$Na^+ (\%) = 100 [(Na^+ + K^+) /(Na^+ + K^+ + Ca^{2+} +Mg^{2+})] \qquad (3)$$

Sodium percentage (Na %) values ranging between 17.34 to 32.58 %. The high percentage of sodium in the irrigation water has dangerous effects on soil. This percentage should not exceed 60[19] (Table 3).

Residual sodium carbonate (RSC)

The excess sum of HCO^-_3in groundwater over the sum of Ca^{2+} and Mg^{2+} also influences the suitability of the groundwater; where Ca^{2+} and Mg^{2+} concentrations are expressed in meq/L, and HCO^-_3 concentrations are expressed in mg/l. The RSC is given by the following equation:

$$RSC = (HCO^-_3 \text{ x}0.0336) – (Ca2^+ +Mg^{2+}) \qquad (4)$$

Magnesium Hazard

An index of magnesium hazard was developed by Paliwal (1972) [20]:

$$\text{Magnesium Ratio} = [(Mg^{2+} / Ca^{2+} + Mg^{2+})] \times 100 \qquad (5)$$

All cations are expressed in meq/L. The MH values range from 24 to 35% and all samples fall below the permissible limit of 50%l indicating no effect on crop yield and decrease in soil alkalinity (Table 2). In the study area all samples are suitable for agricultural uses.

Kelly's ratio

It is a parameter which indicates the suitability of groundwater for irrigation and it is defined as follows:

$$KR= Na^{+} / (Ca^{2+} +Mg^{2+}) \qquad (6)$$

Where, all the ions are expressed in meq/l. Based on Kelly's ratio, water is classified for irrigation. Sodium measured against Ca^{2+} and Mg^{2+} was considered by Kelley (1957) to calculate this parameter. Kelly's ratio more than 1 indicates an excess level of Na+ in water [21]. Therefore, water with the Kelly's ratio less than 1 is suitable for irrigation, while those with a ratio more than 3 are unsuitable for irrigation. Kelly ratio of groundwater in this study area varies from 0.20 to 0.58 with an average of 0.35 (Table3).

Table 3. Na^{+} (%), RSC, MgH and Kr values

ID	Na^{+} (%)	RSC	Mg (%)	Kr
Ain El Fedj	30.58	3.52	35	0.55
Ain Laba	32.05	6.18	28	0.58
Ain Madi	29.07	2.02	31	0.40
BH1	27.07	3.08	34	0.37
BH2	26.19	0.68	29	0.35
BH3	19.37	3.29	24	0.24
BH4	20.48	1.19	25	0.25
B1	20.99	0.60	29	0.26
B2	26.55	-0.42	29	0.36
B3	17,34	-0.68	35	0.20
F1	33.1	1.99	27	0.49

Where Ca^{2+} and $Mg^{2+}$are expressed in meq/l and HCO3 in mg/l. RSC Values ranging between-0.68 to 6.18 mg/l. According To the US department of agriculture water with RSC value more than >2.5 mg/l of RSC is not suitable for irrigation Purposes (Table 3).

4. Conclusions

Groundwater major ions of the Heliopolis aquifers, North of Guelma-Algeria, it is indicated that the most of boreholes and springs are good for drinking and irrigation purposes. Based on the major constituents, groundwater from the studied area corresponded mainly to Ca–Mg–HCO3, Ca-Cl_2 and Ca-SO_4 facies due to the geology of the study area. Based on the Gibbs plot, it is indicated that the rock dissolution as one of the dominant mechanism for hydrogeochemical processes. Saturation indexes show that the most of samples are oversaturation to respect carbonate minerals and under saturation to respect the gypsum mineral. The all major elements in groundwater are safe for drinking and irrigation purposes except calcium have been found above the prescribed permissible limits in few of the samples.

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