JOURNAL OF WATER AND LAND DEVELOPMENT

e-ISSN 2083-4535

Polish Academy of Sciences (PAN), Committee on Agronomic Sciences Section of Land Reclamation and Environmental Engineering in Agriculture Institute of Technology and Life Sciences (ITP) JOURNAL OF WATER AND LAND DEVELOPMENT 2020, No. 46 (VII–IX): 131–139 https://DOI.org/10.24425/jwld.2020.134205

Available (PDF): http://www.itp.edu.pl/wydawnictwo/journal; http://journals.pan.pl/jwld

Received25.08.2019Reviewed18.03.2020Accepted14.04.2020

Assessment of the Hauterivian groundwater quality in zinc mining area for drinking and irrigation uses: Case of Chaabet el Hamra, Algeria

Houria KADA^[], Abdslem DEMDOUM^[]

¹⁾ Larbi Tebessi University, Faculty of Exact Sciences, Natural and Life Sciences, Department of Earth Sciences, Tebessa 12000, Algeria
 ²⁾ Ferhat Abbas University, Institute of Architecture and Earth Sciences, Department of Earth Sciences, Sétif, Algeria

For citation: Kada H., Demdoum A. 2020. Assessment of the Hauterivian groundwater quality in zinc mining area for drinking and irrigation uses: Case of Chaabet El Hamra, Algeria. Journal of Water and Land Development. No. 46 (VII–IX) p. 131–139. DOI: 10.24425/jwld.2020.134205.

Abstract

In order to evaluate the water quality of the Hauterivian groundwater in the zinc deposit of Chaabet el Hamra, Southern Setif region, Algeria, eighteen physico-chemical parameters such as pH, *EC*, *TDS*, Cl⁻, SO₄²⁻, HCO₃⁻, CO₃²⁻, NO₃⁻, Ca²⁺, Mg²⁺, Na⁺, K⁺, and heavy metals Zn, Pb, Fe, Cr, Cd, Mn were analyzed and collected from six different wells in April 2012. The studied groundwater is dominated by HCO_3^- , Ca^{2+} , and Mg^{2+} ions. According to the World Health Organization (WHO) and Algerian standards, all groundwater samples are considered safe and fit for drinking as they fall within the permissible limits. In addition, the Schoeller diagram confirms the best quality water of the Hauterivian groundwater. Gibbs diagram show that the predominant samples fall in the rock-water interaction field, suggesting that water-rock interactions are the major mechanism controlling groundwater chemistry. Assessment of groundwater samples using various water quality indices such as sodium absorption ratio (*SAR*), soluble sodium percentage (*SSP*), residual sodium carbonate (*RSC*), magnesium hazard (*MH*) and Kelly ratio (*KR*) showed that the groundwater in the area has an excellent quality for irrigation purpose. According to Wilcox's diagram, all groundwater samples fall in the C2S1 category, reflecting that they are suitable for irrigation.

Key words: Chaabet el Hamra, drinking water, Hauterivian groundwater, irrigation, quality, Setif

INTRODUCTION

Water is one of the essential requirements for life. All living things need water for their survival. However, the monitoring of water quality is one of the important tools for sustainable development and provides important information for water management [SRINIVASAMOORTHY *et al.* 2009].

For this reason, the quality of water and analysis is an important subject in groundwater studies [AGHAZADEH, MOGADDAM 2010; SUBRAMANI *et al.* 2005], especially, when 80% of diseases in growing countries are directly associated with bad ingesting water and unsanitary conditions [UNESCO 2007].

Groundwater quality data gives important clues to the geologic history of rocks and indications of groundwater recharge, movement, and storage [WALTON 1970]. Groundwater quality depends on the number of factors,

such as general geology, degree of chemical weathering of prevailing lithology, quality of recharge water and inputs from sources other than water-rocks interaction [DOMENI-CO 1972].

The importance of the availability of water with good quality for human health has involved a great deal of interest. It is noted that groundwater is an important water resource for drinking and agriculture uses in the study area. Therefore, the current research is attempted to assess the quality of groundwater and its suitability for drinking and irrigation uses in the Hauterivian aquifer in Chaabet el Hamra, southern Setif (Algeria), using physicochemical analysis and methods. Groundwater in this area is a significant fraction of water supplies, where, more than 70% of the total water for domestic and agricultural purposes. The presence of many Pb and Zn mines in the area leads to deterioration of water quality. This could render serious

© 2020. The Authors. Published by Polish Academy of Sciences (PAN) and Institute of Technology and Life Sciences (ITP). This is an open access article under the CC BY-NC-ND license (https://creativecommons.org/licenses/by-nc-nd/3.0/). threats to human beings, livestock and agricultural production. Therefore, this study is very important as it will assess the quality of groundwater in the region and will provide a baseline for future research initiatives.

STUDY MATERIAL AND METHODS

STUDY AREA

The zinc deposit of Chaabet el Hamra is situated in eastern Algeria (Fig. 1), at 50 km South of Setif in the Ain Azel region. It is located between longitudes 5° to $5^{\circ}30'$ E, and latitudes 36° to 36°30' N. The altitude varies between 950 to 1200 m. It is characterized by a semi-arid climate with average precipitation and temperature of about 328 mm per year and 14.6°C respectively [ONM 2010]. From a geological point of view, the study area is located in the Hodna Mountains, part of the external zone of the Eastern Algeria Alpine Belt [GUIRAUD 1971; VILA 1980]. The Hodna Mountains one of the structural units of the region of Setif (Fig. 2) are part of the autochtonous external zone of Maghrebide Belt [DURAND-DELGA, FONTBOTÉ 1980]. During the Mesozoic, the Hodna was the southern, subsiding margin of the Setif-Constantine carbonate platform, transitional to the Saharian Atlasic trough to the South [VILA 1980]. It is characterized by sedimentary series defined from Triassic to Quaternary [GUIRAUD 1971; VILA 1980]. The Triassic is characterized by gypsum, clay and dolomite formations. The Jurassic is represented by limestones and dolomitic limestones. The Cretaceous formations (Barremian to Cenomanian) are characterized by an alternation of marl and limestone. The Mio-Plio-Quaternary formations are composed of sand, clay, and gravel.

The Setifien/Hodna massifs are characterized by the existence of Pb-Zn deposits and showings, whose best examples are Gustar and Chaabet el Hamra ore deposits. The mineralization is hosted in dolomitic straits of the Hauterivian from infilling fractures in various.



Fig. 1. Geographical location of the study area; source: own elaboration



Fig. 2.Structural map of Setif region; source: geological map of Eastern Algeria, VILA [1980], modified

THE HYDROGEOLOGICAL CONTEXT

The region of Setif extends from El Eulma to Ain Azel. The latter has been the subject of several hydrogeological studies, where, they have identified two important aquifers. The first is the deep aquifer of Barremian and Hauterivian with a thickness of 700 m for both. The latter is recharged by vertically infiltrating meteoric water by fractures and fissures of massifs. The second is the alluvial aquifer (Mio-Plio-Quaternary), about 250 m in thick, comprising an alternation of permeable sediments (sand, gravel, sandy clay).

From the point of view of hydrodynamic (Tab. 1), the average transmissivity of the Hauterivian aquifer is of the order of $6.11 \cdot 10^{-4} \text{ m}^2 \cdot \text{s}^{-1}$ [ENOF 2003].

Sample	Depth (m)	Static level (m)	$\begin{array}{c} Q \\ (dm^{3} \cdot s^{-1}) \end{array}$	Dynamic level (m)	Rabattement (m)
F1	206	80.00	18	150	70.00
F2	233	88.95	17	118	29.05
F3	215	93.00	15	150	57.00
F4	260	84.93	26	120	35.07
F5	190	61.15	20	150	88.85
F6	220	72.80	30	120	47.20

Table 1. Water levels in the study area

Explanations: sampling points as in Fig. 1., Q = discharge. Source: ENOF [2003].

SAMPLING AND ANALYTICAL PROCEDURES

Six different wells (150-200 m of depth) were collected during the month of April 2012 in the study area (Fig. 3). All water samples were stored in polyethylene bottles (250 cm^3) , which were washed before with acid solution and distilled water. At the time of sampling, the bottles were also thoroughly rinsed two times with the drilling water. Before sampling, the pump was allowed to work for 15 min and once the values of water characteristics (T, EC, and pH) reached a constant quantity, then the samples were taken. The water samples were filtered to separate possible suspended solids. Further, to prevent unpredictable variations in water composition, samples were stored in a refrigerator below 4°C. The electrical conductivity (EC) and pH values of the samples were determined at the site of sampling using a portable conductometer (Consort C 5010).



Fig. 3. Location of the sampling sites of the study area; source: extracted from the geological map of the deposit of Chaabet el Hamra [ENOF 2003]

The values of physicochemical parameters of the groundwater samples were compared with guidelines of the World Health Organization [WHO 2008] and the Algerian standards [NA6360 1992] for drinking water, and the standard of Food and Agriculture Organization of the United Nations [AYERS, WESTCOT 1994] for irrigation water (Tab. 2).

Table 2. Guidelines and standards used for assessing groundwater quality for drinking and irrigation purposes (mg·dm⁻³ except for pH)

Parameters	The Algerian standard (NA 6360 [1992])	WHO [2008]	AYERS and WESTCOT [1994]	
pH	6.5-8.5	6.5 to 9.225	8.5	
$EC (\mu S \cdot cm^{-1})$	2800	≤ 1500	3000	
TDS	2000	1500	2000	
SO4 ²⁻	200/400	250	960	
Cl⁻	200/500	200	1063	
HCO ₃ ⁻	-	-	610	
Nitrates (NO ₃ ⁻)	50	20	10	
Ca ²⁺	75/200	200	400	
Mg ²⁺	150	50	60	
Na ⁺	200	100	919	
\mathbf{K}^+	20	12	2	
Zinc	5	3	2	
Lead	0.05	0.01	5	
Iron	0.3	0.3	0.3	
Manganese	0.5	0.4	0.2	
Cadmium	0.01	0.003	0.01	
Chromium	0.05	0.05	0.1	

Source: own elaboration based on WHO [2008]; NA6360 [1992]; AYERS and WESTCOT [1994].

Concentrations of cations such as Na⁺ and K⁺ were determined by flame spectrophotometer (Jenway clinical PFP7) within 24 h of sampling. The calcium (Ca²⁺), magnesium (Mg²⁺), bicarbonates (HCO₃⁻) and chlorides (Cl⁻) ions were analyzed by volumetric titrations, while NO₃⁻ and SO₄²⁻ were determined by ion chromatography. The heavy metals (Pb, Zn, Fe, Cd, Cr, Mn) were detected by the atomic absorption spectrometer (WFX-110B) and total dissolved solids (*TDS*) by drying methods [NOLLET, DE GELDER (eds.) 2007]. All these chemical analyses were performed in the laboratory of the National Agency of Hydraulic Ressources (Fr. Agence Nationale des Ressources Hydrauliques –ANRH), Constantine, Algeria.

RESULTS AND DISCUSSION

HYDROCHEMICAL CHARACTERISTICS

The data of physicochemical parameters of the Hauterivian groundwater from the Chaabet el Hamra deposit are given in Table 3.

Accuracy of the water quality data can be tested by calculating the ionic balance error (IB%) using the Equation (1). It gives an indication of the quality of analysis as well as the possibility of any missing parameter. The data would be rejected if they did not meet the quality criteria. The test is based on the difference percentage defined as:

$$IB\% = 100 \frac{(\Sigma \text{ cations} - \Sigma \text{ anions})}{(\Sigma \text{ cations} + \Sigma \text{ anions})}$$
(1)

The ionic balance should never surpass 10% again [KOUASSI et al. 2013].

For all the water samples, the IB (%) values (Tab. 3) are 10% lower (varied from 3.30 to 7.65 %), and therefore, we consider these analyses reliable.

Samples	pH	EC (μ S·cm ⁻¹)	TDS	Ca ²⁺	Mg^{2+}	Na^+	\mathbf{K}^{+}	HCO ₃ -	CO3 ²⁻	SO4 ²⁻	Cl	NO ₃ ⁻	IB (%)
F1	7.36	740	460	63.64	36.31	29	1	311.1	0	70	40	1	3.30
F2	7.35	690	440	66.85	37.93	17	1	298.9	0	60	35	5	4.54
F3	7.30	730	454	74.74	42.35	19	1	311.1	0	82	40	3	6.15
F4	7.22	750	474	77.19	42.6	19	1	323.3	0	88	40	1	5.44
F5	7.23	770	522	77.97	44.85	20	1	292.8	0	94	50	5	7.65
F6	7.39	720	450	72.25	42.71	20	1	311.1	0	86	40	1	5.76
Min	7.22	690	440	63.64	36.31	17	1	292.8	0	60	35	1	3.30
Max	7.39	770	522	77.97	44.85	29	1	323.3	0	94	50	5	7.65
Mean	7.325	735	457	73.495	42.475	19.5	1	311.1	0	84	40	2	5.47

Table 3. Physicochemical parameters analysed in groundwater samples from the study area (mg·dm⁻³ unless otherwise cited)

Explanations: EC = electrical conductivity, IB = ionic balance error. Source: own elaboration.

WATER PHYSICAL PARAMETERS

The pH of water is an important indication of its quality and provides information in many types of geochemical equilibrium of solubility calculations [HEM 1986]. All the groundwater samples are falling in the range of 7.22 to 7.62 with a mean of 7.3 (Tab. 3), which shows the low alkalinity. It is miles recognized that the buffering manner of calcite and dolomite are dominated by using for pH varies from 6.5 to 7.5 [GELLER *et al.* 2000].

However, the observed values of the pH of the Hauterivian groundwater are within the permissible limits of WHO guidelines and Algerian standard for drinking (Tab. 2). As well, the water of the study area is suitable for irrigation, where the recommended value for irrigation water is from 6.5 to 8.4 [AYERS, WESTCOT 1994]. Irrigation water with a pH over the normal range may cause a nutritional imbalance or may contain toxic ion [AL-OBAIDY *et al.* 2014].

TDS of all the groundwater samples are subsiding in the range of 440 to 522 mg·dm⁻³ with an average of 457 mg·dm⁻³ (Tab. 3), which are inside of the permissible limits for drinking [NA 6360 1992; WHO 2008] and irrigation uses [AYERS, WESTCOT 1994]. Based on the *TDS* classification in the water [HEM 1986], all groundwater samples are labeled inside the freshwater class.

Electrical conductivity (*EC*) is the most important parameter in determining the suitability of water for drinking and irrigation uses, due to the fact excessive *EC* results in the formation of saline soil [ESMAEILI, MOORE 2012]. For the *EC* in the Hauterivian groundwater of the study area, all the values are failing between 690 and 770 μ S·cm⁻¹ with a mean of 735 μ S·cm⁻¹ (Tab. 3). Thus, we can conclude that the groundwater of the area is acceptable for drinking [NA 6360 1992; WHO 2008] and irrigation uses [AYERS, WESTCOT 1994].

WATER CHEMICAL PARAMETERS

Calcium concentration ranges between 63.64 and 77.97 mg·dm⁻³ with a mean of 73.49 mg·dm⁻³ (Tab. 2). The calcium content in the study area is within the permissible limits for drinking [NA 6360 1992; WHO 2008] and irrigation uses [AYERS, WESTCOT 1994]. Calcite and dolomite are responsible for enriching the groundwater with calcium ions [KIM, YUN 2005].

The magnesium concentration in the groundwater samples ranges between 36.31 to 44.85 $mg \cdot dm^{-3}$ and with a mean of 42.47 $mg \cdot dm^{-3}$ (Tab. 3). The magnesium content in the study area is within the permissible limits for drinking [NA 6360 1992; WHO 2008] and irrigation uses [AYERS, WESTCOT 1994].

Sodium concentration in the Hauterivian groundwater samples varied from 17 to 29 mg·dm⁻³ with an average value of 19.5 mg·dm⁻³ (Tab. 3). All of the groundwater samples fall within the permissible limit of drinking water standard [NA 6360 1992; WHO 2008]. Furthermore, sodium content is the most troublesome of the major ions and important factor in irrigation water quality evaluation [AYERS, WESTCOT 1994].

Chloride ion is a predominant natural form of chlorine and is extremely soluble in water. The major source of chloride in natural water is particularly evaporation sedimentary rocks [PRADHAN, PIRASTEH 2011]. In the study area, chloride ion content in all the groundwater samples varied from 35 to 50 mg·dm⁻³ with a mean value of 40 mg·dm⁻³ (Tab. 3). These values are within the permissible limits for drinking [NA 6360 1992; WHO 2008] and irrigation uses [AYERS, WESTCOT 1994].

The concentration of HCO_3^- ion found in the groundwater samples of the study area ranged from 292.8 to 323.3 mg·dm⁻³ with an average of 311.1 mg·dm⁻³ (Tab. 3). Therefore, the groundwater in the examination zone is overwhelmed by HCO_3^- , which records for over 54% of the all-out anions and cations. These values are inside of the permissible limits for drinking [NA 6360 1992; WHO 2008] and irrigation uses [AYERS, WESTCOT 1994].

Nitrates and K^+ have a minimal offer in absolute concentrations of anions and cations with 1% of the particle fixation aggregate.

The predominance of HCO_3^- , Ca^{2+} , and Mg^{2+} in groundwater are mainly due to the dissolution carbonates rocks of the Cretaceous formations (Barremian to Cenomanian).

PRINCIPAL COMPONENTS ANALYSIS

Multivariate statistical analysis is an impulse that has been specifically created for considering and breaking down data sets.

In groundwater research, multivariate statistical analysis is a quantitative approach to groundwater classification

Variable	pН	EC	TDS	Ca ²⁺	Mg ²⁺	Na ⁺	\mathbf{K}^+	HCO ₃ ⁻	SO_4^{2-}	Cl⁻	NO_3^-
pН	1.00										
EC	-0.71	1.00									
TDS	-0.74	0.88	1.00								
Ca ²⁺	-0.77	0.58	0.62	1.00							
Mg^{2+}	-0.59	0.54	0.61	0.96	1.00						
Na^+	0.29	0.31	0.04	-0.56	-0.53	1.00					
\mathbf{K}^+	0.00	0.00	0.00	0.00	0.00	0.00	1.00				
HCO ₃ ⁻	-0.04	0.04	-0.38	0.06	-0.06	0.16	0.00	1.00			
SO_4^{2-}	-0.60	0.79	0.70	0.87	0.91	-0.15	0.00	0.13	1.00		
Cl	-0.57	0.87	0.95	0.60	0.66	0.11	0.00	-0.40	0.77	1.00	
NO_3^-	-0.23	-0.12	0.31	0.14	0.14	-0.50	0.00	-0.87	-0.16	0.24	1.00

Table 4. Pearson's correlation matrix for the physicochemical parameters of groundwater samples

Explanations: EC = electrical conductivity, TDS = total dissolved solids. Source: own elaboration.

which allows the grouping of groundwater samples and making correlations between samples and their chemical parameters [CÜNYET *et al.* 2002].

The interrelations between physicochemical parameters in groundwater were inspected using Pearson's correlation matrix (Tab. 4).

The Pearson correlation coefficients show that pH displays a negative correlation with all parameters and the strong correlation between *TDS*, Cl⁻ and *EC* (r = 0.88, r = 0.87 respectively), *TDS* and Cl⁻ (r = 0.95).

Surrounded by cations, just Ca^{2+} and Mg^{2+} determine a negative connection (r = -0.56, r = -0.53 distinctly) with Na⁺ which can be indicated that they got from various sources. The highest positive correlation (r = 0.96) exists somewhere in the range of Ca^{2+} and Mg^{2+} which can be translated as they got from the same sources (dissolution of carbonate minerals).

For anions, a high positive correlation between SO_4^{2-} and Cl^- (r = 0.77). HCO_3^- shows a negative or feeble correlation with Cl^- , SO_4^{2-} and NO_3^- . The correlation coefficients between anions and cations show that Na⁺ has a powerless correlation with HCO_3^- and Cl^- . These feeble or negative connections translated the non-identical source for relating ions.

HEAVY METALS

The term heavy metal includes metals with a density superior to 5 g·cm⁻³, with the exception of earthy alkaline. The accompanying components are referred to as substantial metals: bismuth (Bi), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), tin (Sn), iron (Fe), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), lead (Pb), and zinc (Zn).

Table 5. Heavy metals analyzed in groundwater samples from the study area (mg·dm⁻³)

Metal	F1	F2	F3	F4	F6		
Zn	0	0.007	0.035	0.048	0.016		
Pb	not detectable						
Fe	0.073	0.071	0.085	0.307	0.141		
Cr	not detectable						
Mn	0.009	0.014	0.014	0.017	0.018		
Cd	not detectable						

Source: own elaboration.

As this area study is mine for the Zn exploitation, the investigations of substantial metal are in this way required to affirm the disintegration or non-disintegration of the Zn in the waters of the Hauterivian groundwater. The investigation of substantial metals affirms their low nearness in these waters (Tab. 5).

MECHANISMS CONTROLLING THE GROUNDWATER CHEMISTRY

Piper diagram is widely used to understand problems concerning the geochemical evolution of groundwater [KARMEGAM *et al.* 2011]. The diagram consists of three distinct fields including two triangular fields and a diamond-shaped field. The cations expressed as a percentage of total cations in meq·dm⁻³ as a single point on the left triangle while anions plot is in the right triangle [PIPER, 1944]. In order to understand the chemical evolution mechanism of the Hauterivian groundwater in the mining area in the Chaabet el Hamra, Piper trigram was drawn (Fig. 4).

As shown in Figure 4, the Piper diagram classified all water samples into $Ca^{2+}-Mg^{2+}-HCO_3$ type which could be because of the disintegration of carbonate rocks from the adjacent sedimentary sequences.



Fig. 4. Piper diagram for groundwater samples; source: own study

The reaction between aquifer minerals and groundwater has a significant role in water quality, which is also useful to understand the genesis of groundwater [CEDER-STORM 1946]. Commonly, different processes and mechanisms control groundwater chemistry. Therefore, Gibbs plots are used to understand and differentiate the influences of rock-water interaction, evaporation and precipitation on water chemistry [GIBBS 1970]. It is recommended a realistic portrayal to comprehend significant procedures controlling the groundwater, in view of total dissolved solids (*TDS*) versus Na⁺/(Na⁺ +Ca²⁺) for cations and Cl⁻/(Cl⁻ + HCO₃⁻) for anions. Gibbs diagrams showed that rock weathering mainly controlled the major ions chemistry of the Hauterivian groundwater in the study area (Fig. 5).



Fig. 5. Gibbs plot of Hauterivian waters; *TDS* = total dissolved solids; source: own study

GROUNDWATER FOR DRINKING USES

The SCHOELLER [1962] diagram is correspondingly used for evaluating the quality of consuming water. It is based on eight chemical parameters (Ca²⁺, Mg²⁺, Na⁺, *TDS*, TH, Cl⁻, SO₄²⁻ and HCO₃⁻). It represents a semilogarithmic diagram of the concentrations of the groundwater samples of the study area. Points on the equally spaced lines represent the concentration of each ion in each sample and points are connected by a line. Overall *TDS* and TH and according to this diagram, water is classed into six classes: permissible, intermediate, unpleasant, very unpleasant, good and non-potable. Accordingly, groundwater samples from the Chaabet el Hamra place inside good categories (Fig. 6).

The relative tendency of ions in mg·dm⁻³ shows $Ca^{2+} > Mg^{2+} > Na^+$ for cations and $HCO_3^- > Cl^- > SO_4^{2-}$ for anions. The diagram in this study supports the Piper diagram revealed Ca^{2+} , Mg^{2+} , and HCO_3^- as dominant cation and anion respectively.



source: own study

GROUNDWATER FOR IRRIGATION USES

Indices such as sodium absorption ratio (*SAR*), soluble sodium percentage (*SSP*), residual sodium carbonate (*RSC*), permeability index (*PI*), magnesium hazard (*MH*), and Kelly ratio (*KR*) are significant parameters for determining the suitability of groundwater for irrigation purposes [AGHAZADEH, MOGADDAM 2010; QIU *et al.* 2019].

SODIUM ABSORPTION RATIO (SAR)

Sodium concentration plays a significant responsibility in evaluating the groundwater quality for irrigation because sodium causes a reduction in the soil permeability. The sodium hazard of irrigation water can be well understood by *SAR*, which determines its utility for agriculture [AL OBAIDY *et al.* 2014].

Sodium absorption ratio (*SAR*) is defined by Equation (2), where all particle fixations are in meq \cdot dm⁻³ [RICHARD (ed.) 1954] – Table 6.

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}}$$
(2)

|--|

Samples	Ca ²⁺	Mg^{2+}	Na ⁺	\mathbf{K}^+	HCO ₃ ⁻	CO3 ²⁻	SO_4^{2-}	Cl⁻	NO_3^-
F1	3.176	2.988	1.261	0.026	5.100	0	0.729	1.130	0.016
F2	3.336	3.121	0.739	0.026	4.900	0	0.625	0.989	0.081
F3	3.730	3.485	0.826	0.026	5.100	0	0.854	1.130	0.048
F4	3.852	3.505	0.826	0.026	5.300	0	0.917	1.130	0.016
F5	3.891	3.691	0.870	0.026	4.800	0	0.979	1.412	0.081
F6	3.605	3.515	0.870	0.026	5.100	0	0.896	1.130	0.016

Source: own elaboration.

The *SAR* values range from 1.17 to 2.05 in the Hauterivian groundwater. It is reported that if the value of SAR is less than 10, the water is with excellent quality for irrigation [RICHARD (ed.) 1954]. Consequently, all the water samples are excellent for irrigation.

WILCOX DIAGRAM

WILCOX [1955] diagram is one of the most important classifications in this study. Within the Wilcox diagram, the horizontal axis is selected to water salinity, while the vertical one to the SAR. As shown in Figure 7, all samples are inside the C2S1 category, meaning "barely salinesuitable for irrigation" (Tab. 7).



Fig. 7. Wilcox diagram for studied groundwater; source: own study

 Table 7. Summary of the Wilcox's classification classes for irrigation water

Water class	Quality for irrigation
C1S1	freshwater - absolutely harmless for irrigation
C1S2, C2S2, C2S1	slightly saline - suitable for irrigation
C1S3, C2S3, C3S1,	saline - suitable for irrigation with appropriate
C3S2, C4S2, C4S1	treatment
C1S4, C2S4, C3S4,	very saline - harmful for irrigation
C4S4, C4S3, C4S2,	
C4S1	

Source: WILCOX [1955].

SOLUBLE SODIUM PERCENTAGE (SSP)

SSP is also used to assess sodium hazard. Additionally, SSP known as %Na is calculated by Equation (3), where all ion concentrations are in meq \cdot dm⁻³ [WILCOX 1955] – Table 6.

$$\% Na = 100 \frac{Na+K}{Ca+Mg+Na+K}$$
(3)

The calculated values of *SSP* varied from 7.70 to 13.05%. It is reported that if the value of *SSP* is less than 20, the water is with excellent quality for irrigation [WIL-COX 1955]. Consequently, all the water samples are representing an excellent quality on the use of this groundwater in irrigation.

RESIDUAL SODIUM CARBONATE (RSC)

RSC has been used to determine the hazardous effect of carbonate and bicarbonate on the quality of water for irrigation. *RSC* is a calculated value expressing the excess in CO_3^{2-} and HCO_3^{-} content, which remains after the consummation of Ca^{2+} and Mg^{2+} content. The *RSC* was calculated according to Equation (4) recommended by EATON [1950].

$$RSC = (HCO_3 + CO_3) - (Ca + Mg)$$
 (4)

All the ion concentrations are in $meq \cdot dm^{-3}$ (Tab. 6).

The calculated *RSC* values range from -2.78 to -1.06, which indicated that all of the groundwater samples have *RSC* less than zero. It is reported that if the value of *RSC* is less than 10, the water is excellent for irrigation [EATON 1950]. Thus, all the water samples are representing an excellent quality for irrigation purposes.

PERMEABILITY INDEX (PI)

The *PI* was also used for assessing sodium hazard and the suitability of water for agricultural use. *PI* is calculated by the method suggested by DONEEN [1962] in the following equation:

$$PI = \frac{Na + \sqrt{HCO_3}}{Ca + Mg + Na + K} 100$$
(5)

All ions are expressed in $meq \cdot dm^{-3}$ (Tab. 6).

The *PI* values in this study ranged from 13.92 to 20.29%. It is reported that if the value of *RSC* is less than 25%, the water is unsuitable for irrigation [DONEEN 1962]. However, the Hauterivian groundwater in the study area is unsuitable for irrigation purposes.

MAGNESIUM HAZARD (MH)

SZABOLCS and DARAB [1964] are proposed to identify and calculated the magnesium hazard (*MH*) for irrigation water as in the following formula:

$$MH = \frac{Mg}{Ca + Mg} 100 \tag{6}$$

 Ca^{2+} and Mg^{2+} ions are in meq·dm⁻³ (Tab. 6).

The values of MH have been calculated in the water samples of the study area varied between 35.56 to 37.15%. It is reported that if the value of MH is less than 50, the water is safe and suitable for irrigation [PALIWAL 1972]. However, the Hauterivian groundwater can be classed as suitable for irrigation.

KELLY RATIO (KR)

The *KR* has calculated the usage of Equation (7), where Na⁺, Ca²⁺ and Mg²⁺ ions are in meq·dm⁻³ [KELLY 1940] – Table 6.

$$KR = \frac{Na}{Ca + Mg} \tag{7}$$

If the *KR* value is less than one, the amount of Na⁺ in the water is feeble, and the water is suitable for irrigation [KELLY 1940]. In water samples of the study area, the *KR* is less than one (0.08–0.15). Therefore, Hauterivian groundwater is appropriate for irrigation.

CONCLUSIONS

The Hauterivian groundwater in Chaabet el Hamra, Zn deposit, South of Setif region is immensely important for water supply in both urban and rural areas. As compared with the WHO guidelines and Algerian standard for drinking water to the Hauterivian groundwater, the values of analyzed parameters (physicochemical and heavy metals) of all groundwater samples are in the limits, and Schoeller diagram showed that the Hauterivian groundwater in the study area is good for drinking use.

Results show that the Hauterivian groundwater of Chaabet el Hamra is dominated by Ca^{2+} , Mg^{2+} and HCO_3^- components. Gibbs diagram showed that rock (Cretaceous formations) weathering mainly controlled the major ions. Similarly, the principal components analyse highlighted positive connections between some ions, which can be translated as they got from the same sources. Whereas, the negative correlations advise the non-identical source for relating ions.

Based on the classification of irrigation water according to sodium adsorption ratio (1.17-2.05), soluble sodium percentage (7.7-13.05) and residual sodium carbonate (from -2.78 to -1.06) values, all the samples location are excellent for irrigation purposes.

Similarly, the magnesium hazard (35.5–37.1) and Kelly ratio (0.08–0.15) values suggested that the samples are suitable for irrigation water, and all of the groundwater samples can be used directly without treatment.

ACKNOWLEDGEMENTS

We thank anonymous reviewers for the valuable suggestions, which helped us improving the quality of our paper.

REFERENCES

- AGHAZADEH N., MOGADDAM A.A. 2010. Assessment of ground water quality and its suitability for drinking and agricultural uses in the Oshnavieh area, northwest of Iran. Journal of Environmental Protection. Vol. 1. No. 1 p. 30–40. DOI 10.4236/ jep.2010.11005.
- AL OBAIDY A.H.M.J., KADHEM A.J., HAMIZA N.H., AL MASH-HADY A.A.M. 2014. Assessment of ground water quality for drinking and agricultural uses in Mouqdadiya District, Diyala, Iraq. Engineering and Technology Journal. Vol. 32. Part (A). No. 12 p. 2921–2936.
- AYERS R.S., WESTCOT D.W. 1994. Water quality for agriculture. Irrigation and Drainage Paper. No. 29. Rev. 1, M-56. Rome, Italy. FAO ISBN 92-5-102263-1 pp. 174.
- CEDERSTORM D.J. 1946. Genesis of groundwater in the coastal plain of Virginia. Economic Geology. Vol. 41. Iss. 3 p. 218– 245. DOI 10.2113/gsecongeo.41.3.218.
- DOMENICO PA. 1972. Concepts and models in groundwater hydrology. New York. McGraw-Hill. ISBN 0070175357 pp. 405.

- DONEEN L. 1962. The influence of crop and soil on percolating water. In: Proceeding 1961 biennial conference on groundwater recharge. 26–27.06.1962 Berkeley, CA, USA p. 156–163.
- DURAND-DELGA M., FONTBOTE J.M. 1980. Le cadre structural de la Méditerranée occidentale. En : Géologie des chaines alpines. Issues de la Téthys. [The structural framework of the western Mediterranean. In: Geology of the Alpine chains born of the Tethys]. Mémoire du B.R.G.M. No. 115. Colloque C5. 26^{ème} congrés géologique international. Paris. p. 67–85.
- EATON F.M. 1950. Significance of carbonates in irrigation waters. Soil Science. Vol. 69. Iss. 2 p. 123–134.
- ENOF 2003. Rapport final sur l'hydrogéologie du gisement de Chaabet el hamra [Final report on the hydrogeology of the Chaabet el hamra deposit]. Rapport interne pp. 40.
- ESMAEILI A., MOORE F. 2012. Hydrogeochemical assessment of groundwater in Isfahan province, Iran. Environmental Earth Sciences. Vol. 67 p. 107–120. DOI 10.1007/s12665-011-1484-z.
- GELLER W., FRIESE K., HERZSPRUNG P., KRINGEL R., SCHULTZE M. 2000. Limnology of sulphur-acidic mining lakes. II Chemical properties: The main constituents and buffering systems. Internationale Vereinigung für Theoretische und Angewandte Limnologie: Verhandlungen. Vol. 27 p. 2475– 2479. DOI 10.1080/03680770.1998.11901686.
- GIBBS R.J. 1970. Mechanism controlling world water chemistry. Science. Vol. 170. Iss. 3962 p. 1088–1090. DOI 10.1126/ science.170.3962.1088.
- GUIRAUD R. 1971. Aperçu sur les principaux traits structuraux du Hodna et des régions voisines [Overview of the main features of Hodna and neighboring regions]. Bulletin de service de l'Algérie. No. 41. Nouvelle série. Publication du service géologique de l'Algérie pp. ???.
- HEM J.D. 1986. Study and interpretation of the chemical characteristics of natural water. Water-Supply Paper. No. 2254. Alexandria. Washington, DC. United States Government Printing Office pp. 263.
- KARMEGAM U., CHIDAMBARAM S., PRASANNA M.V., SASIDHAR P., MANIKANDAN S., JOHNSONBABU G., DHEIVANAYAKI V., PARAMAGURU P., MANIVANNAN R., SRINIVASAMOORTHY K. 2011. A study on the mixing proportion in groundwater samples by using Piper diagram and Phreeqc model. Chinese Journal of Geochemistry. Vol. 30. Iss. 4 p. 490–495. DOI 10.1007/s11631-011-0533-3.
- KELLY W.P. 1940. Permissible composition and concentration of irrigated waters. In: Proceedings of the ASCF. Vol. 66 p. 607–613.
- KIM K., YUN S.T. 2005. Buffering of sodium concentration by cation exchange in the ground water system of a sandy aquifer. Geochemical Journal. Vol. 39. Iss. 3 p. 273–284. DOI 10.2343/geochemj.39.273.
- KOUASSI A.M., MAMADOU A., AHOUSSI K.E., BIEMI J. 2013. Simulation de la conductivité électrique des eaux souterraines en relation avec leurs propriétés géologiques : Cas de la Côte d'Ivoire [Conductivity simulation of groundwater in relation to its geological properties: Case of the Ivory Coast]. Revue Ivoirienne des Sciences et Technologie. Vol. 21–22 p. 138-166.
- NA 6360 1992. Normes algériennes [Algerian norms]. Ed. Ianor.
- NOLLET L.M.L., DE GELDER L.S.P. (eds.) 2007. Handbook of water analysis. 2nd ed. Boca Raton. CRC Press. ISBN 10 1904445365 pp. 769.
- ONM 2010. Organisation nationale de la météo (la station d'Aïn Azel) [Weather data from Aïn Azel station]. [unpublished].
- PALIWAL K.V. 1972. Irrigation with saline water. Monograph. Vol. 2. New Delhi. Water Technology Centre IARI pp. 198.

139

- PIPER A.M. 1944. A graphical procedure in the geochemical interpretation of water analysis. Eos, Transactions American Geophysical Union. Vol. 25. Iss. 6 p. 914–928. DOI 10.1029/TR 025i006p00914.
- QIU H., GUI H., CUI L., PAN Z., LU B. 2019. Hydrogeochemical characteristics and water quality assessment of shallow groundwater: A case study from Linhuan coal-mining district in northern Anhui Province, China. Water Supply. Vol. 19. Iss. 5 p. 1572–1578. DOI 10.2166/ws.2019.030.
- RICHARDS L.A. (ed.) 1954. Diagnosis and improvement of saline and alkali soils. Agriculture Handbook. No. 60. Washington, DC. USDA p. 69–82.
- SCHOELLER H. 1962. Les eaux souterraines [Groundwater]. Paris. Masson Cie. pp. 642. DOI 10.1002/iroh.19640490118.
- SRINIVASAMOORTHY K., CHIDAMBARAM S., SARMA V.S., VASAN-THAVIGAR M., VIJAYARAGHAVAN K., RAJIVGANDHI R., ANANDHAN P. and MANIVANNAN R. 2009. Hydrogeochemical characterization of ground water in Salem District of Tamilnadu, India. Research Journal of Environmental and Earth Sciences. Vol. 1. Iss. 2 p. 22–33.

- SUBRAMANI T., ELANGO L., DAMODARASAMY S.R. 2005. Groundwater quality and its suitability for drinking and agricultural use in Chithar River Basin, Tamil Nadu, India. Environmental Geology. Vol. 47 p. 1099–1110. DOI 10.1007/ s00254-005-1243-0.
- SZABOLCS I., DARAB C. 1964. The influence of irrigation water of high sodium carbonate content of soils. Proceedings of 8th International Congress. Iss. 2 p. 803–812.
- UNESCO 2007. Water portal newsletter. Water related diseases. No. 161 p. ??-??.
- VILA J.M. 1980. Chaîne alpine de l'Algérie orientale et des couffins algéro-tunisiens [Alpine chain of eastern Algeria and Algerian-Tunisian borders]. PhD Thesis. Université P. et M. Curie, Paris VI pp. 665.
- WALTON W.C. 1970. Groundwater resource evaluation. New York. McGraw Hill Book Co. pp. 664.
- WHO 2008. Guidelines for drinking-water quality: Incorporating first and second addenda, recommendations. 3rd ed. Vol. 1. Geneva. WHO Press. ISBN 978 92 4 154761 1 pp. 668.
- WILCOX L.V. 1955. Classification and use of irrigation water. Circular. Iss. 969. Washington, DC. USDA pp. 19.