



Determination of scaling, corrosion tendencies and water type in the Annaba-El Tarf aquifers, Northeastern of Algeria

Samia Bounab^{*1,3}, Houria Bousnoubra-Kherici², Abdelamid Saou³, Nassima Sedrati¹

¹Department of Geology, Faculty of Sciences of the Earth, University Badji Mokhtar, Annaba, Algeria

²Department of Hydraulic, Faculty of Engineering Sciences, Laboratory of Soil and Hydraulic, University Badji Mokhtar, Annaba, Algeria

³Research Laboratory in Applied Hydraulics and Environment, Faculty of Technology, University of Bejaia road of Targa Ouzemour, Bejaia, Algeria

Article published on May 29, 2017

Key words: Groundwater types, Hydrochemistry, Scaling potential, Corrosiveness, Annaba-Algeria.

Abstract

In this present study, 34 Hydrochemical data of groundwater samples in Annaba – El-Tarf areas were examined with an aim to assess the Scaling and corrosion tendencies of water using Langelier and Ryznar indexes. Hydrochemical and statistical methods such as Piper and Chidah diagrams were also applied to the data set. The results obtained show that 73.53% of the samples are classified into intolerable corrosion, 20.59% of the samples have little scale or slightly corrosive. The samples show the same property with respect to the two indexes. Hydrochemical characteristics show that Cl⁻ and HCO₃⁻ are the major anions and Na⁺ and Ca²⁺ are the major cations in water of the studied area. However 23.52% of the samples exceed the desirable limit of Cl⁻, 20.58% of Na⁺, and 8.82% of them exceed that of SO₄²⁺. Groundwater types were assessed and compared with Piper and Chdha diagrams, it was found that Na-Cl is the dominant type, in both methods.

*Corresponding Author: Bounab Samia ✉ bounsam2006@yahoo.fr

Introduction

Groundwater is the primary source of water for domestic, agricultural and industrial used in many countries and its contamination has been recognized as one of the most serious problems (Kamegam U *et al*, 2010). The corrosion is highly widespread that causes progressively the pollution of groundwater. This phenomenon has been extensively studied by several authors (Agatemor *et al*, 2008, Atasoy and Yesilnacar, 2010, Abyaneh *et al*, 2011, Singh *et al*, 2012, Kurdi *et al*, 2015), particularly in the Mediterranean basin, with the extension of semi-arid conditions. In fact the water overexploitation, low recharge and anthropogenic actions (industrial and agricultural) which tend to increase the concentrations of certain metals in tap water. Corrosion can affect public health and the cost of providing safe water.

The mineralization is acquired by the interaction of water with the host rocks (Boudoukha, 2015). Therefore, it contains, in the dissolved phase several elements that can lead to chemical reactions in contact with pipes, tanks or equipments constituting the network of water supply. Nevertheless, these materials are likely to be degraded by the waters transported. This phenomena lead to a deterioration of the installations and sometimes to an alteration of the organoleptic quality or water physico-chemistry (dissolution of lead, copper, nickel, colored waters by the dissolved iron...).

Indeed the study area, the groundwater reservoirs are easily affected by pollution. However, the assessment of groundwater vulnerability to pollution has been extensively studied by several authors (Kherici, 1993, Djabri L, 1996, Debieche TH, 2002, Kherici *et al*, 2009, Attoui *et al*, 2014, Sedrati *et al*, 2016).

This new assessment methodology leads to two objectives: the first one is to determine the corrosivity or scale formation potential of the groundwater using Langelier and Ryznar Indexes, the second one to assess the groundwater chemistry using piper and Chidhaplots.

Materials and methods

Description of the studied Area

The studied area is located in the north- east of Algeria; it includes 2 wilayas (Provinces) it is limited to the north by the Mediterranean Sea, south by wilayas of Guelma and Souk ahras, to the east by the borders between Algeria-Tunisia and to the west by the wilaya of Skikda (Fig. 1). The region is known by its intense industrial and agricultural activity. It constitutes the lower plain of the Wadis (streams) Ressoul, Seybouse, Bounamoussa and Khebir with different geomorphological formations (mountains, lakes, wadis and plains) where it is characterized by intense vegetative cover especially at the mountains' level.

According to (Hilly, 1962, Villa1980), the study area is part of geological entire Eastern North Algerian Tell. There are two types of terrain; one metamorphic (Cristallophylein) of primary age presented by the Eddough Massif in the West, and the other sedimentary age (Tertiary to Quaternary) almost occupying the totality of Annaba plains. The latter is the seat of permeable aquifers formation constituting important water reservoirs specially Annaba aquifers (superficial and deep groundwater) aquifers El-Tarf (dunes of El-Chatt, and massive dune Bouteldja. The region is subjected to Mediterranean climate defined by a cold and rainy winter and a hot, dry summer, the average annual rainfall, real evapotraspiration are respectively 700,500 mm/year (Halimi *et al*, 2016).

Sample collection and analysis

A total of 34 groundwater samples from boreholes located at Bouteldja, les salines, El Tarf and Berrahal, used for human consumption (Fig. 1) were collected. In order to remove any stagnant water in boreholes, samples were collected after a pumping time as long as possible until the electrical conductivity (EC) and pH values stabilized. Temperature, pH, and EC were measured in situ using portable instruments (EXSTIK II pH/conductivity EC. 500). All chemical analyses were carried out at the Algerian Water laboratory of Annaba (ADE Annaba). Alkalinity was measured using acid titration.

Samples were first filtered through 0.45 μm membrane filters, with samples for minor and trace elements acidified using concentrated analytical-grade ultrapure to prevent adsorption and chemical precipitation. All water samples were stored at 4°C until analysis. The water samples were analyzed for major and trace elements. Anions analyzed include bicarbonate, sulfate, chloride and nitrate. Cations analyzed include sodium, magnesium, calcium and potassium. Trace elements analyzed include Fe and Al. Calcium, Mg, Na, K, Fe and Al were analyzed by atomic absorption spectrophotometry and HCO₃ and Cl by H₂SO₄ and AgNO₃ titration, respectively. SO₄ was analyzed by turbidimetric method and the NO₃ by colorimetry with a UV-visible spectrophotometer. Standard solutions for the above analysis were prepared from the respective salts of analytical reagent grades. The accuracy of the chemical analysis was verified by calculating ion-balance errors, the errors were generally within ± 10%.

Methods of data processing

The results of the physico-chemical analyzes have been treated by the methods of statistical analysis (with the software XLSTAT 2008). The approach used to determine the index of LANGELIER and Ryznar, is primarily established from the program "Equilibre1" developed by (Pierre RAVARINI, 2007) and represented by the method of the box plot Tukey (Le Guen M, 1999), which allows to represent schematically a statistical distribution in particular to locate the extreme points. These indexes determine the nature of water, aggressive, neutral or incrustant. The second approach is based on the Hydrochemical characteristics of the groundwater, which requires the use of the Piper and Chidah diagram realized with the software Diagram, to identify water type and Hydrochemicalfacies.

Description of corrosion index

Langelier Saturation Index LSI was given by Langelier in 1936 to predict the water tendency to precipitate or dissolve CaCO₃. The LSI can be calculated by taking the difference between the measured pH of water (pHw) and saturation pH for CaCO₃ (pHs).

The Langelier Index (LI) is probably the most widely used as indicator of water scale potential or of water corrosively. LI is a thermodynamic parameter that determines the scale formation potential which is related to the precipitation or dissolution of calcium carbonate (Withers, 2005). Calcium carbonate dissociates in the water as follows the relationship between CO₃²⁻ and HCO₃⁻ can be given by the second dissociation constant of the carbonic acid (Hamrouni & Dhahbi, 2002).



Eventually, Langelier Index (LI) is found as: LI = pHw - pHs. If a water has a negative LI value (pH < pHs), it is under saturated with respect to calcium carbonate and is potentially corrosive. Conversely, for waters with a positive LI (pH > pHs), the water is super saturated with CaCO₃ and the water has the potential to form scale. Saturated water has a LI of zero (pH = pHs) (Al-Rawajfeha *et al*, 2005). The Langelier Index shows the direction of the driving force but does not indicate if the over saturation is high enough to initiate crystallization. John Ryznar modified the LSI in 1944. Similar to LSI, Ryznar, therefore, suggested an index, which attempts to quantify the relationship between CaCO₃ saturation state and scale formation (Carrier Air Conditioning Company, 1965). Ryznar Index (RI) was found as: RI = 2 - pHs - pH. The evaluation of the Langelier and Ryznar Indexes are shown in Tables 1 and 2.

Table 1. Class of Langelier Saturation Index (Carrier Air Conditioning Company, 1965).

Langelier saturation index	Tendency of water
LSI < - 2	Intolerable corrosion
-2.0 < LSI < -0.5	Serious corrosion
-0.5 < LSI < 0	Slightly corrosive but non-scale forming
LSI = 0	Balanced but pitting
0 < LSI < 0.5	Slightly scale forming and corrosive
0.5 < LSI < 2	Scale forming but non corrosive

Table 2. Class of Ryznar Stability Index (Carrier Air Conditioning Company, 1965).

Ryznar Stability Index	Tendency of water
RSI 4.0 – 5.0	Heavy scale
RSI 5.0 – 6.0	Light scale
RSI 6.0 – 7.0	Little scale or corrosion
RSI 7.0 – 7.5	Corrosion significant
RSI 7.5 – 9.0	Heavy corrosion
RSI >9.0	Intolerable corrosion

Results and discussion

The table 3 shows the statistics of Langelier and Ryznar indexes. These are represented by the box plot of Tukey (Fig. 2 and 3).

From the analysis based on Langelier index (Fig. 2), it was seen that 73,53% of the samples was found to be intolerable corrosive, 17,65% slightly scale forming and corrosive, 8,82% showing scale forming but non corrosive.

Whereas based on Ryznar stability index (Fig. 3), none of the samples were found to be heavy scaling, 2.94 % of them have light scale. Which characterize a significant corrosion are 2.94% and 20.59% which indicates a little scale or slightly corrosive. An alarming fact is that 73.53% of the samples are found to be of intolerable corrosion. It is very clear that the results of LSI are reasonably comparable with the RSI values and the samples show the same property with respect to the two indexes. According to the fig. 4, the results show that the groundwater’s exhibiting corrosive/significant corrosive property is the ones which are on the acidic side (pH< 7). Based on LSI values nearly 91.18% of the samples are corrosive, while the RSI values indicate that nearly 76.5% of the samples exhibit significant to heavy corrosion. The correlation of pH and LSI presented in Fig. 4, indicate clearly that alkaline waters are scale forming and acidic waters corrosive in nature.

Table 3. Descriptive Statistics of Langelier and Ryznar indexes.

	Statistics	Sum of the weights	Min	First Quartile	Average	3 rd Quartile	Max	Average
Index of Langelier	Bouteldja	22	-4.67	-3.99	-3.71	-3.53	-2.62	-3.73
	Salines	5	0.28	0.38	0.41	0.51	0.66	0.45
	El Tarf	4	-3.58	-3.45	-3.14	-2.11	0.18	-2.42
	Berrahal	3	0.37	0.38	0.39	0.68	0.97	0.58
Index of Ryznar	Bouteldja	22	11.41	13.32	13.57	14.1	15.15	13.60
	Salines	5	6.03	6.28	6.31	6.34	6.56	6.31
	El Tarf	4	7.16	11.07	12.76	13.27	13.62	11.60
	Berrahal	3	5.85	6.18	6.51	6.52	6.54	6.30

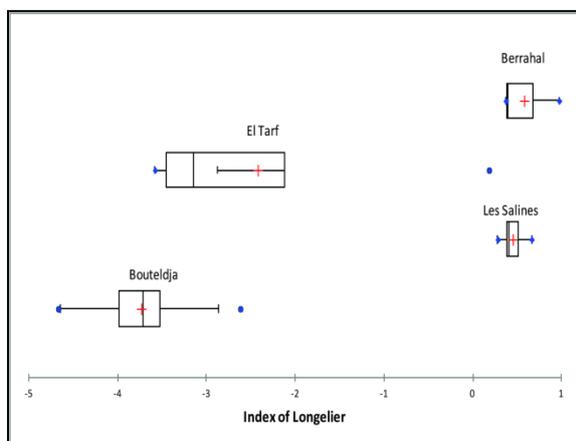


Fig.2. Representation of Langelier index with method of Tukey Box.

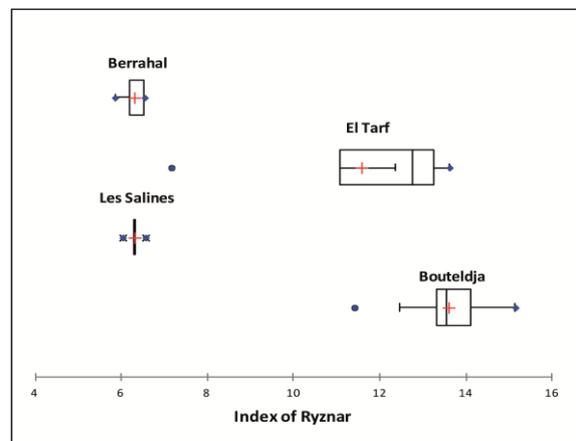


Fig.3. Representation of Ryznar Index with method of Tukey Box.

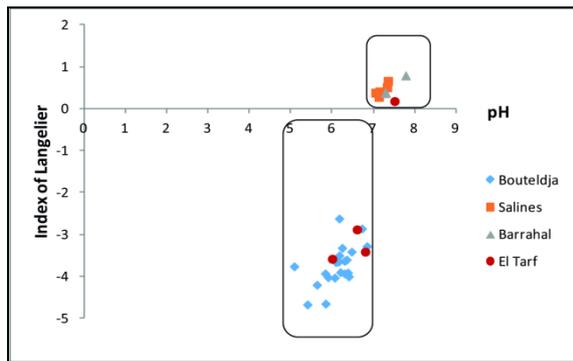


Fig.4. Correlation pH- index of Langelier plot.

The mean, standard deviation (SD), minimum (Min.) and maximum (Max.) values of the 14 physicochemical parameters of 34 groundwater samples were measured and presented in Table 4. The mean concentrations of major ions in the study area are within the WHO guidelines for drinking water. The electrical conductivity of groundwater samples ranges from 120 to 2740 $\mu\text{S}/\text{cm}$ with a mean value of 641.91 $\mu\text{S}/\text{cm}$. The pH ranges between 5.08 and 7.78 with a mean value of 6.47. The mean temperature of waters was 19.83 °C. These analyses shows that the Cl^- and HCO_3^- are the major anions and Na^{2+} and Ca^{2+} are the major cations in groundwater of study area.

The relative abundance of the cations and anions respectively are $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$ (Table 4). The maximum Na^{2+} and Cl^- concentrations are 417 mg/l and 691.33 mg/l respectively, they are however, higher than respective WHO standards. The presence of these elements is related to the dissolution of the formations licks and the effect of the marine intrusion.

The mean Mg^{2+} and K^+ concentrations in the groundwater are 18.907 mg/l and 2.24 mg/l, respectively. The value of the Ca^{2+} in the studied area ranges between 2 and 208.42 mg/l. The presence of bicarbonate ions HCO_3^- in the groundwater is derived from carbon dioxide in the atmosphere, soils and by dissolution of carbonate minerals. Bicarbonate ion represents the second dominance anion in the study area. Its concentration in the study area ranges between 2.22 and 448.35 mg/l. The extensive and important occurrences of sulfate ions in the investigated water are dissolution of evaporate minerals such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4). The value of SO_4^{2-} in the studied area ranges between 5.76 and 412.8 mg/l.

Table 4. Statistics of the various physicochemical parameters.

Parameters	WHO	Min	Max	Mean	SD
T	< 25	14.5	24.20	19.83	2.43
pH	6.5 – 8.5	5.08	7.78	6.47	0.63
EC	180-1000	120.00	2740.00	641.91	882.17
NH_4^+	0.5	0.04	0.58	0.11	0.11
NO_2^-	0.2	0.01	0.11	0.03	0.02
NO_3^-	≤ 50	1.10	21.26	7.64	5.26
Ca^{2+}	200	1.60	208.42	45.5	68.3
Mg^{2+}	150	0.91	99.65	18.91	28.5
Na^+	≤ 200	11.70	417.00	83.36	111.73
K^+	≤ 12	0.20	4.70	2.24	1.16
Fe^+	≤ 0.3	0.01	3.37	0.45	0.72
Al^+	≤ 0.3	0.01	0.32	0.06	0.06
HCO_3^-	450	2.22	448.35	107.87	165.23
Cl^-	≤ 250	24.82	691.33	134.10	189.67
SO_4^{2-}	≤ 250	5.76	412.80	57.08	96.75
CO_2	< 10	6.47	148.12	50,69	32,94

All values are in mg/l except pH, T (°C) and EC ($\mu\text{S}/\text{cm}$).WHO (2011).

However the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio of groundwater from this area also supports the dissolution of calcite and dolomite present in the aquifer (Fig. 5). In fact the ratio $\text{Ca}^{2+}/\text{Mg}^{2+} = 1$, dissolution of dolomite should occur, whereas a higher ratio is indicative of greater

calcite contribution (Maya and Loucks, 1995). Higher $\text{Ca}^{2+}/\text{Mg}^{2+}$ molar ratio (> 2) indicates the dissolution of silicate minerals, which contribute calcium and magnesium to ground water (Katz *et al*, 1998). Results presented in Fig. 5 reveal that all of the

samples have a ratio greater than 2 (52.9 %) indicate the effect of silicate minerals. Results of the samples closer to the line ($Ca^{2+}/Mg^{2+} = 1$) indicate the dissolution of dolomite (20.62%). Whereas those with values greater than 1 indicate the dissolution of calcite (26.7 %). At most 23.52% of the samples exceed the desirable limit of Cl^- (250 mg/l), 20.58% of Na^{2+} (200 mg/l), and only 8.82% of them exceed that of SO_4^{2-} (250 mg/l) (WHO, 2011).

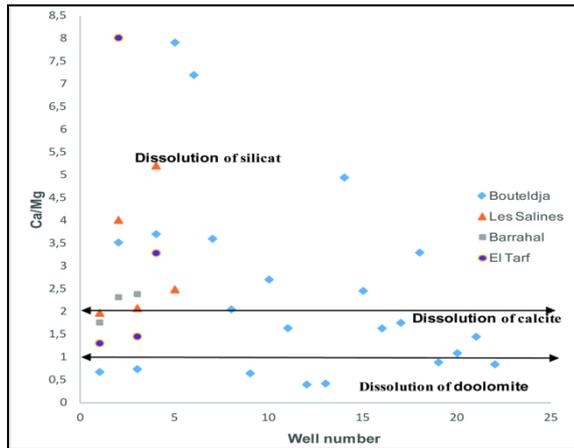


Fig. 5. Plot Ca^{2+}/Mg^{2+} vs well number.

Hydrochemical diagram proposed by (Chadha, 1999) has been applied in this study; the processes suggested are indicted in each of the four quadrants of the graph. These are broadly summarized as:

- Group 1: $Ca-HCO_3$ recharging waters
- Group 2: $Ca-Mg-Cl$ type reverse ion- exchange waters
- Group 3: $Na-Cl$ type end-member waters (sea water)
- Group 4: $Na-HCO_3$ type base ion-exchange waters

Study water types using Chadha's hydrochemical diagram (Fig.6), shows that the majority of samples 82.35% are in group 3 ($Na-Cl$), waters are typical sea water mixing. 11.76 % of samples are in group 2 (reverse ion-exchange. Minor representations of samples are also found in group 1 and group 4 with one sample in each group (Fig.6).

Evaluation of the water types using Piper diagram (Fig. 7) and Chidha plot (Fig. 6), show that the majority of the samples represents the $Na-Cl$ type of water. We note the dominance of sodium chloride facies (82.35%).

The $Na-HCO_3$ type of water, the percentage of samples in this category is respectively 8.82 % and 2.94%. It is the same for the $Ca-HCO_3$ type of water, the percentage of samples in this category is respectively 5.88 % and 2.94 %.

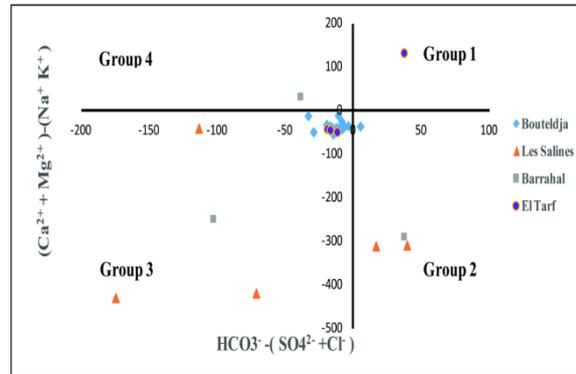


Fig. 6. plot $(Ca^{2+} + Mg^{2+}) - (Na^+ K^+)$ vs $HCO_3^- - (SO_4^{2-} + Cl^-)$.

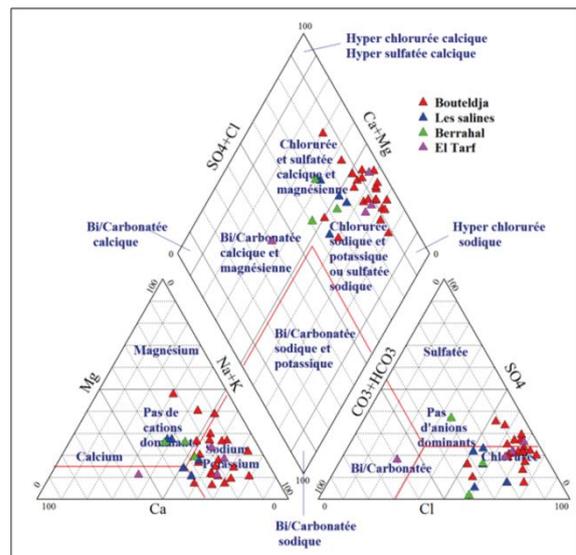


Fig. 7. Piper plot shows groundwater samples.

Conclusion and recommendation

The quality, scaling potential, and corrosiveness of groundwater were evaluated in Annaba-El Tarf area, northeastern Algeria. Langelier saturation index and Ryznar stability indexes have underlined that 73.53% of the samples are classified into intolerable corrosion, 20.59% of the samples have little scale or slightly corrosive, 5.88 % of the samples are found to be light scale or indicating significant corrosion. The samples show the same property with respect to the two indexes.

Results of the hydrochemistry analyses show that the Cl^- and HCO_3^- are the major anions and Na^+ and Ca^{2+} are the major cations in groundwater of the studied area. However the results show that 23.52% of the samples exceed the desirable limit of Cl^- (250 mg/l), 20.58% of Na^+ (200 mg/l), and only 8.82% of them exceed that of SO_4^{2-} (250 mg/l). Ground water types were assessed and compared with Piper and Chdha diagrams, 82.35% of the water samples were Na-Cl types, in both methods.

The scaling as well as corrosive nature of groundwater renders them unfit for regular domestic use. Thus, waters with corrosive property cannot be transported in metallic pipes. It thus becomes highly imperative for the civic authorities to pay attention to this and reduce the adverse effects that may be caused.

References

- Abyaneh HZ, Varkeshi MB, Mohammadi K, Howard K, Marofi S.** 2011. Assessment of groundwater corrosivity in Hamedan Province Iran using an adaptive neuro-fuzzy inference system. *Geosciences Journal* **15**, 433 – 439.
- Agatemor C, Patrick A, Okolo O.** 2008. Studies of corrosion tendency of drinking water in the distribution system at the University of Benin. *Environmentalist* **28**, 379–384.
- Al-Rawajfeha AE, Gladeb H, Ulrichc J.** 2005. Scaling in multiple-effect distillers: The role of CO_2 release. *Desalination* **182**, 209-219.
- Atasoy, Yesilnacar MI.** 2010. Effect of high sulfate concentration on the corrosivity: a case study from groundwater in Harran Plain, Turkey. *Environ Monit Assess* **166**, 595–607.
- Attoui B, Kherici N, Kherici-Bousnoubra H.** 2014. Use of the new method for determining the vulnerability and risk of pollution of major groundwater reservoirs in the region of Annaba-Bouteldja (NE Algeria). *Environmental Earth Sciences* **72**, 891-903.
- Boudoukha A, Athamna M, Benaabidat L.** 2015. Etude du Potentiel Hydrothermal de Hammam Sokhna. EST ALGERIEN. *Larhyss Journal* **24**, 161-174.
- Carrier Air Conditioning Company.** 1965. Handbook of Air Conditioning System Design. New York, McGraw-Hill Books.
- Chadha DK.** 1999. A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data. *Hydrogeol Journal* **7(5)**, 431-439.
- Debieche TH.** 2002. Evolution of groundwater quality (salinity, nitrogenizes and heavy metals) under the effect of pollution salt works, agricultural and industrial, application to the low plain of Algerian north-eastern Seybouse. Doctorat Thesis, University Franche-Comte; 235p.
- Djabri L.** 1996. Mechanism of sey bouse water pollution and vulnerability geological, industrial, agricultural and urban origins. Doctorat Thesis, University of Annaba, 176 p.
- Halimi S, Baali F, Kherici N, Rechachi H, Younis AK.** 2016. Impact of agricultural activities on the evolution of nitrate and nitrite levels in ground water of Annaba plain (North East of Algeria). *Journal of Biodiversity and Environmental Sciences (JBES)*. Vol. 9.N°. **3**, 120-124.
- Hamrouni B, Dhahbi M.** 2002. Calco-carbonic equilibrium calculation. *Desalination* **152**, 167-174.
- Hilly J.** 1962. Etude géologique du massif de l'Edough et du Capde Fer (Est-Constantinois). Publications du service de la Carte géologique de l'Algérie. Bulletin N° 19, 408 pages.
- Katz BG, Coplen TB, Bullen TD, Davis JH.** 1998. Use of chemical and isotopic tracers to characterize the interaction between groundwater and surface water in mantel dKarst. *Groundwater* **35(6)**, 1014-1028.

- Kherici N, Derradji EF, El Kand Y.** 2009. Vulnerability to pollution and Urban Development of the massive dune of Bouteldja, Northeaster Algeria. *Geographica Technica* **1**, 1-7.
- Kherici N.** 1993. Vulnérabilité à la pollution chimique des eaux souterraines d'un système de nappes super posées en milieu industrie et agricole (Annaba-la-Mafragh) Nord-Est algérien. Doctoral thesis 170-189.
- Kurdi M, Ferdows M S, Maghsoudi A.** 2015. Sensitivity of Corrosion and Scaling Indices Based on Ions; Case Study Iran. *Water Qual Expo Health* **7**, 363-372.
- LE Guen M.** 1999. De l'importance de l'image, *Courrier des Statistiques*, n°90, INSEE, p7-9.
- Maya AL, Loucks MD.** 1995. Solute and isotopic geochemistry and groundwater flow in the Central Wasatch Range, Utah. *Journal of Hydrology* **172**, 31-59.
- Sedrati N, Djabri L, Chaffai L.** 2016. Evaluating groundwater pollution and assessing the vulnerability. Case of massive dune of Bouteldja, Algeria. *Journal of Biodiversity and Environmental Sciences (JBES)*. Vol.9.N°. **5**, P. 129-136.
- Singh VK, Bikundia DS, Sarswat A, Mohan D.** 2012. Groundwater quality assessment in the village of Lutfullapur Nawada, Loni, District Ghaziabad, Uttar Pradesh, India. *Environ Monit Assess* **184**, 4473-4488.
- Villa JM.** 1980. The Alpine chain Eastern borders Algeria Algerian-Tunisiens doctoral thesis of natural sciences. Pierre and Marie Curie Paris VI University p. 665.
- Withers A.** 2005. Options for recarbonation remineralisation and disinfection for desalination plants. *Desalination* **179**, 11-24.
- World Health Organization (WHO).** 2011. Guidelines for Drinking-water Quality. 4th edition Geneva, Switzerland.