

Groundwater quality from the El Aarjate zone (Morocco)

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Abstract

The main aim of this study is to assess the groundwater quality from El Aarjate zone (Morocco), a zone with high agricultural activity, and to identify its physicochemical characteristics. The water sampling was carried out on 25 wells, during summer and winter seasons. The parameters measurement which have been performed are: pH, electrical conductivity (EC), bicarbonates (HCO₃), nitrates (NO₃), sulfate (SO₄²⁻), magnesium (Mg²⁺), calcium (Ca²⁺) and sodium (Na⁺). The temporal and spatial monitoring of the chemistry of these waters have shown that the hydro-chemical quality depends on the lithological nature of the underlying formation and, secondly, on anthropogenic pollution (in our case: use of nutrient rich fertilizers).

Keywords: groundwater, wells, Arjaate zone, quality, physicochemical parameters

1. Introduction

Water is an essential element for life of all living beings, thus, it deserves a special attention, especially because in modern world it is highly threatened by human activities. Indeed, the non-rational use of fertilizers and pesticides and the lack of awareness about the environmental protection, generate the pollutants, which could affect the physicochemical and biological quality of water bodies and aquifers. The groundwater is a resource of drinking water mostly required in the worldwide. Therefore, various studies [1-4] have shown that, the groundwater plays vital importance, either for consumption as drinking water or for using of other purposes such as irrigation. However, the deterioration of water quality is becoming increasingly important in the world [2]. This phenomenon is due to the human activities which have contributed to their increasing [1, 5-6].

In Morocco, particularly in our study area (Aarjate) some fertilizers and pesticides are used, such as the fertileader, parcos, boom super, corefol k46, n-p-k. Thus, the physicochemical of water could be influenced with this income. In addition, the largest part of water heritage is in the ground. The contamination of this compartment (water) is coming from the industrial development, the demographic growth has been increasing in the country, and the development of the agro-livestock sector [[7, 8]. The challenge that all Moroccan regions are facing, in particularly rural areas, is to protect the quality of groundwater resources. Indeed, the groundwater pollution is one of the most disturbing aspects, and their use in consumption is a health hazard [9].

The aim of our study was to evaluate the physicochemical quality of groundwater in the El Aarjate zone, dominated by agricultural activities and individualized breeding. The majority of people of El Aarjate zone use this groundwater, without treatment, both for irrigation and for their daily needs.

2. Materials and Methods

2.1. Sampling site

The El Aarjate zone (Fig.1) is located 25 km from the City of Rabat - the capital of the Kingdom of Morocco, between the coordinates 34.031° and 33.944 ° N, 6.667° and 6.571° E. This zone is covering an area of about 151.86 Km², with an average elevation of 130.84 m above sea level. The climate belongs to the semi-arid of Mediterranean climate influenced with the Atlantic sea. It is dominated by agriculture and cattle breeding. The zone has been divided in 3 areas considering the agriculture activities intensity: Souk LARBAA ESSEHOUL (1), Barrage Sidi Mohammed Ben Abdellah (2), and Bab El Had (3).

2.2. Sampling and laboratory analysis

The sampling periods were in summer (June-September 2013), (July & September 2015) and in winter (December 2013, January - February 2014), which are both the highest seasons (dry and wet, respectively). The groundwater samples were taken from 25 wells, in bottles of 1.5 litters, which were well washed with the distilled water. They were kept in laboratory 24h after sampling, in conditions of constant temperature and not in direct light before the analysis.

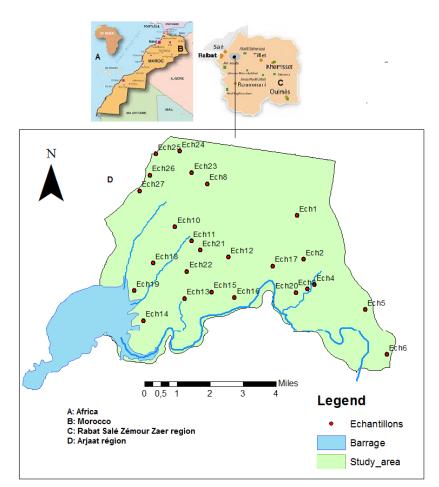


Figure 1. Map of El Aarjate zone, Morocco, area of sampling and the sampling points

The measurement of electrical conductivity (Cond) and hydrogen ion concentration (pH) were performed in situ using Jenway 3510 pH-meter. The Calcium (Ca^{2+}), Magnesium (Mg^{2+}) and Chloride (Cl), were measured by titrimetric method. The Nitrates (NO₃), Carbonates (HCO₃), Sulfates (SO₄) determinations were performed using Jasco V-530 UV/VIS Spectrophotometer and the Sodium (Na) were performed using Flame Photometer Jenway Clinical PFP 7. Those measurements were performed according to the AFNOR standards [10]. The composition of soil: clay (p_A_t), sand (p_S_t) and silt (p_L_t) percentages were calculated using pipette ROBINSON method [11] at Institut National de Recherche Agronomique, Rabat.

2.3. Statistics and mapping

The mapping of the study area and of physicochemical parameters distribution was performed using ArcGIS 10.1 software. The distribution maps were generated using Ordinary Kriging interpolation method [12, 13]. The statistical analysis was performed using SPSS 20 software, and for comparison analysis, World Health Organization (WHO) thresholds were used. For the assessment of the relationship degree between the physicochemical parameters, the PCA (Principal Component Analysis) was used and the correlations have been analyzed with bivariate method. The values were standardized to z-scores before correlation. Chemical analysis has been made by the Piper diagram, built with the diagram software, in order to identify the various water classes [14].

3. Results and discussion

In Table 1, the soil characteristics of the zone are presented. The results of the physicochemical parameters are summarized in Table 2, where the concentration's range and the mean for groundwater sample, and percentage of wells exceeding the thresholds (% exceeding) are shown. The % of wells exceeding was calculated for all elements as the percentage of values which are exceeding the WHO limits from the total number of samples.

Table 1. The particle size characteristics of soil of the El Aarjate zone

	%A	% LF	% LG	% SF	%SG	% CaCO3
Souk Larbaa Essehoul (1)	13.90	7.10	17.00	41.80	14.80	5.40
Barrage Sidi Med Ben Abdellah (2)	7.60	6.00	11.10	55.90	17.70	1.80
Bab El Had (3)	5.90	3.80	4.80	56.90	27.60	1.00

[%]A: The percentage of the clay content; % LF and % LG are respectively: the fine silt, and the coarse silt; %SF and %SG are respectively: the fine sand and the coarse sand.

a. Hydrochemical mapping

The physicochemical analysis has shown that the pH of the groundwater in the El Aarjate zone is neutral and ranged in WHO threshold values recommended 6.5-8.5 [16]. However, we find the very slight decline during winter period (Fig. 2), particularly as observed during the same season; the organic matter is in increasing. This change in pH probably comes from the mineralization of organic matter which is present in the water, and releasing H^+ ions. The increasing in the organic matter during the winter season due to the contribution of the rest of plant, the rain and the infiltration of the water through the agricultural soil.

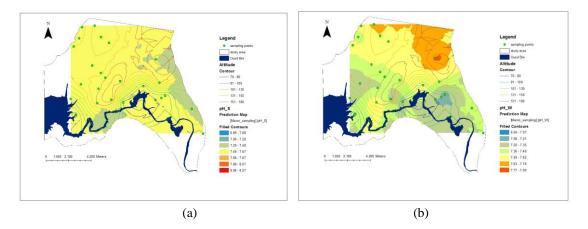


Figure 2. Distribution maps of pH (a) summer and (b) winter in El Aarjate zone, Morocco

The electrical conductivity (EC) measurements are used to assess the amount of dissolved salts in the water, its mineralization. The data recorded during both study seasons are higher in certain sampling points (Fig. 3). This

strong mineralization of groundwater depends on the composition ions through the soil, the organic matter degradation in the same compartment and on the location of wells according to the human activities.

	Area: Souk LAF	RBAA ESSE	HOUL	Area: Barra Abdellah	ge S. Med	Area:Bab H	El Had	Morocco's norms [15]	WHO & EPA norms [16], [17
$a_{n=25}$		N1	= 8		= 11	N3	= 6		
pН		Summer	Winter	Summer	Winter	Summer	Winter		
	Min (mg/l)	6.89	6.94	7.12	7.14	7.24	7.27		
	Max (mg/l)	8.00	7.90	8.27	7.79	7.83	7.75	6.5 – 9	6.5 - 8.5
	Mean (mg/l)	7.45	7.40	7.59	7.38	7.55	7.55		
	% exceeding ^b	0.00	0.00	0.00	0.00	0.00	0.00		
Cond.	Min (μ S/cm ²)	998.00	551.00	553.00	600.00	566.00	580.00		
	Max (µS/cm ²)	2570.00	2880.00	2580.00	2490.00	786.00	778.00	2700	1500
	Mean(µS/cm ²	1480.13	1510.75	1108.64	1130.00	648.2	638.83		
	% exceeding ^b	37.50	37.50	9.09	9.09	0.00	0.00		
Ca ²⁺	Min (mg/l)	60.12	63.33	44.98	41.68	41.68	43.29		
	Max (mg/l)	252.40	178.36	236.47	170.34	100.2	115.42	100	70
	Mean (mg/l)	118,22	114.13	93.28	92.79	55.45	62.26		
	% exceeding ^b	75.00	87.50	54.55	72.73	33.33	16.67		
Mg ²⁺	Min (mg/l)	12.16	15.08	11.43	11.01	7.30	6.81		
	Max (mg/l)	95.82	97.52	60.80	82.69	39.40	18.00	50	50
	Mean (mg/l)	54.84	48.31	28.32	25.81	14.11	10.84		
	% exceeding ^b	62.50	37.50	909	9.09	0.00	0.00		
Cl	Min (mg/l)	39.05	46.15	39.05	39.05	65.80	54.01		
	Max (mg/l)	745.50	745.50	702.09	599.95	98.85	99.40	300	200
	Mean (mg/l)	299.10	283.56	238.82	187.15	68.63	66.99		
	% exceeding ^b	62.50	50.00	36.36	36.36	0.00	0.00		
NO ₃ ⁻	Min (mg/l)	7.18	7.67	12.32	19.85	21.18	22.37		
	Max (mg/l)	85.59	68.58	62.46	74.25	80.63	68.58	50	50
	Mean (mg/l)	27.27	25.81	30.80	42.17	48.04	53.14		
	% exceeding ^b	12.50	12.50	9.09	18.18	33.33	66.67		
HCO ₃ -	Min (mg/l)	140.30	207.40	164.70	201.78	170.80	164.70		
	Max (mg/l)	463.60	457.50	353.80	353.80	286.70	250.10	200	200
	Mean (mg/l)	321.78	325.21	252.04	256.80	223.67	213.20	200	200
	% exceeding ^b	75.00	100.00	90.91	100.00	66.67	66.67	-	
SO ₄	Min (mg/l)	6.15	7.35	5.02	6.64	4.78	20.10		
	Max (mg/l)	97.75	133.75	107.40	84.35	18.52	36.96	250	200
	Mean (mg/l)	54.29	62.96	25.04	25.26	9.91	9.82	250	200
	% exceeding ^b	0.00	0.00	0.00	0.00	0.00	0.00	-	
Na^+	Min (mg/l)	32.80	32.50	23.30	22.56	27.40	25.40		
1.14	Max (mg/l)	240.00	230.00	269.50	148.50	101.60	99.00	200	150
	Max (mg/l)							200	150
	% exceeding ^b	120.94 25.00	115.56 25.00	105.44 27.27	82.37 0.00	59.10 0.00	56.57 0.00	4	

Table2. The concentration's range, average and percentage of samples exceeding the World Health Organization (WHO) thresholds (% exceeding) for the physicochemical parameters for groundwater in El Aariate zone. Morocco

b % exceeding = percentage of locations where WHO thresholds are exceeded

Indeed, the septic systems could be the source of this important conductivity value in the wells: p6, p20 and p21, which are over of the WHO threshold values (1500 S/cm) [16-18]. The slightly higher levels during the winter season could be explained by the remobilization and leaching of salts accumulated in soil [19]. As well as, it's shown in Figure 3, we have seen that the conductivity values are high in the Souk Al Arbaa Essehoul area with 37% of the wells that are over the WHO standard, it could be explained by waste household from the Allal El Bahraoui village located in north of this area, which would contaminate the environment. Then the soil of this area has shown that the carbonate of calcium is in dominance $(CaCO_3)$ which can increase the conductivity in groundwater (Table 1).

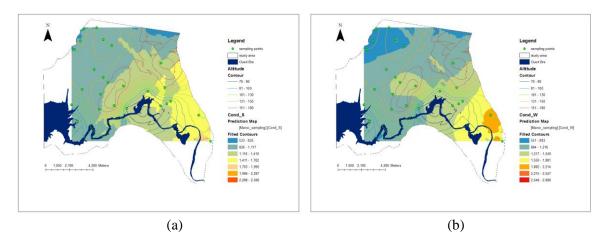


Figure 3. Distribution Map of E.C, (a) summer and (b) winter in El Aarjate zone, Morocco

The bicarbonates (HCO₃) in groundwater are coming largely from rocks and soil composition, especially from the calcareous sedimentary rocks [20]. In the El Aarjate zone, the content of bicarbonates increases from NW to SE of the zone (Fig. 4). This increasing is based on the content of the ground carbonate of calcium (CaCO₃) (Table 1). Therefore, the CaCO₃ with the water and carbon dioxide become the bicarbonates [21, 22], according to the following formula: $2CaCO_3 + CO_2 + H_2O \Leftrightarrow Ca^2 + 2HCO_3$. Whoever, it was found that during wet season, there is a high bicarbonate content in groundwater, is explained by the same chemical reaction taking place in soil, when it is raining, and then it infiltrates and reaching to the groundwater.

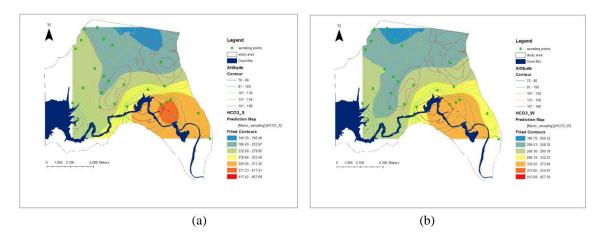


Figure 4. Distribution maps of HCO₃ concentration (a) summer and (b) winter, El Aarjate zone, Morocco

Sodium (Na) is ubiquitous in groundwater, but the concentration variation is depending of the soil and rock type through leaching. It could be also coming from other sources, such as the leaching of geological compositions containing sodium chloride and / or the decomposition of silicate rocks. However, the authors have specified that, the presence of sodium with other minerals in groundwater play a role on the characteristics of the electric conductivity [7, 23, 24]

In the El Aarjate zone, the Sodium concentration also increases from N.W to S.E (Fig. 5). Indeed, in the Souk Larbaa Essehoul area, the sodium concentration, present 25% of sampling sites which are exceeding to the EPA and WHO threshold values (150 mg/l) [18], during two seasons. In Barrage Sidi Med Ben Abdellah area, 27.27% sampling site are above this threshold values but only in summer, while in the 3rd area, Bab El Had, the sodium concentration is the lowest compared with the first two areas.

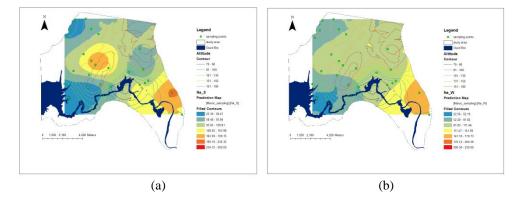


Figure 5. Distribution maps of Na concentrations (a) summer and (b) winter, El Aarjate zone, Morocco

The Chlorides (Cl) are also ubiquitous in environment by various forms; they are associated either with the Sodium (Sodium Chloride) or with Potassium (Potassium Chloride). According to the various studies, chlorides in groundwater come from the weathering and leaching of sedimentary rocks and soils, anthropogenic activities, the infiltration of irrigation water and the dissolution of salt deposits [23, 25, 26].

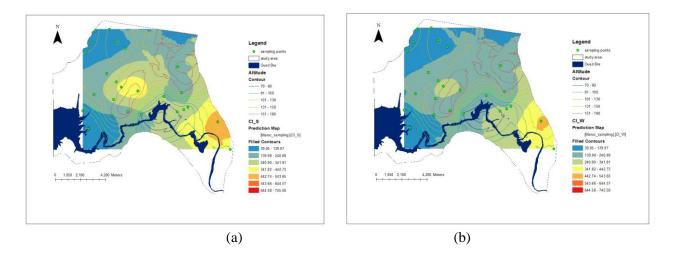


Figure 6. Distribution maps of Cl concentrations (a) summer & (b) winter, El Aarjate zone, Morocco

In our case, we have seen a variation from one region to another with the chlorides concentration in increasing from NW-SE. The results have shown that, for the area (1), a slight decrease of chloride concentration from summer to the wet season (Fig. 6), which is explained that in summer the ions are more concentrated than in winter season, therefore, in winter there is a dilution according the precipitation quantities. This decreasing level of chlorides from wet season to dry season was seen in other studies carried out in parts of Morocco [23, 27]. The Concentration of chlorides beyond the WHO threshold values (200mg/L) [16] found in this study, (62% and 50% was winter) in area (1) and 36.36% (summer and winter) in area (2), could be from the fertilizers used by farmers in these regions. However, these values are all below of the maximum permissible threshold value for the drinking water in Morocco (750 mg/L) [15].

The Magnesium (Mg^{2+}) and Calcium (Ca^{2+}) ions influence the hardness of groundwater. The sources of these ions are in the lithology of the aquifer and hydrolysis of silicate minerals [2, 28]. We note, for both Mg^{2+} and Ca^{2+} , that the Souk Larbaa Essehoul area has the most sites exceeding the maximum value in two seasons, followed by the barrage Sidi Mohamed Ben Abdellah, while in Bab El Had area the low overshoot has been noted only for Ca^{2+} . Indeed, the concentrations of these ions in the groundwater of El Aarjate zone increase from NW to SE (Fig. 7 and Fig. 8) depending of the soil type crossing. In fact, the locations where high values of $CaCO_3$ have been found the Mg^{2+} and Ca^{2+} are also important (Table 1).

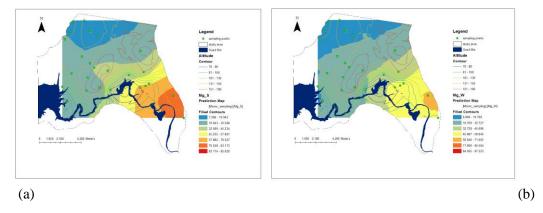


Figure 7. Distribution maps of Mg²⁺ concentrations (a) summer and (b) winter, El Aarjate zone, Morocco

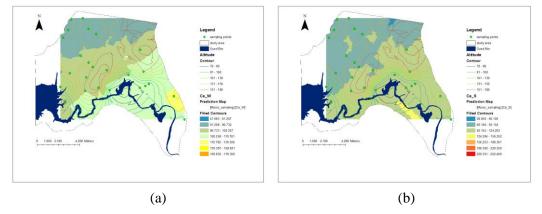


Figure 8. Distribution maps of Ca²⁺ concentrations (a) summer & (b) winter, El Aarjate zone, Morocco

The nitrates in groundwater have various sources such as from natural origin or decomposition of organic matter (plant and/or animal), and, also from human activities, like the fertilizers [19, 27, 29].

In the El Aarjate zone, the concentration of nitrate (NO₃), varies from one season to another and then change from one to another area. But unlike the other parameters, the nitrates increase from SE to NW. In Bab El Had area most of wells are exceeding the Moroccan and WHO threshold values (50 mg/L)[16], followed by the barrage Sidi Mohamed Ben Abdellah area, and the Souk Larbaa Essehoul. Indeed, there is a high content of nitrate in the Northwest area, where the soil is mostly sandy-type (Table 1). The spatial distribution (Fig. 9) has shown in particular that the concentration increases in the winter season, which can be explained by easier infiltration of rainwater into the sandy soil than in the other soil types [14, 30]. These high levels have probably origin from use of the nutrient rich fertilizers and livestock activities.

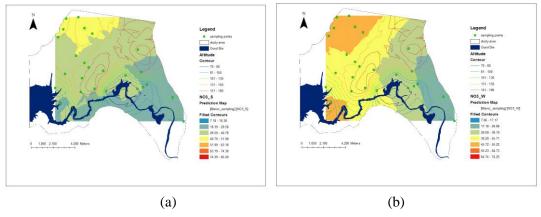


Figure 9. Distribution maps of NO₃ concentrations (a) summer & (b) winter, El Aarjate zone, Morocco

The various studies [7, 20], have shown that, the Sulfates (SO_4) in groundwater have taken origin from the runoff and seepage through the gypsum land or from the intervention of bacterial activity (rhodothiobactéries, chlorothiobactéries, etc.), which is made by the oxidation of Dihydrogen Sulfide (H2S),"toxic form of sulfate"[6]. They can also take origin from the urban pollution, or industrial and agricultural.

During the wet period, the concentration of sulfate is increasing for some wells, specially, in the South East area of the El Aarjate zone (Fig. 10). Indeed, the sulfates concentration in groundwater of Souk Larbaa Essehoul area, could take origin from the rocks of the basement. It is explained by the nature type of the clay soil, and the rate of $CaCO_3$ higher than in the other areas (Table 1). In this area, the soil probably contains the sulfates ions, which are accommodated in the form of calcium sulfates, magnesium sulfates or sodium sulfates [6, 20]. According to WHO threshold values, and the Moroccan threshold values, the concentrations of sulfates in the all Areas of El Aarjate zone are below the required limit value (200 mg/L) [15, 16].

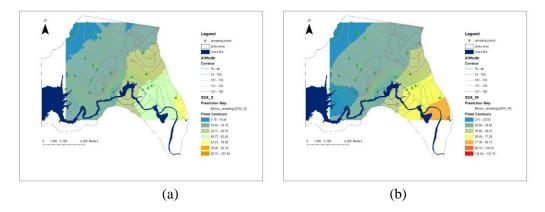


Figure 10. Distribution maps of SO₄ concentrations (a) summer & (b) winter, El Aarjate zone, Morocco

b. Principal Component Analysis

In this study, the statistical analysis with Principal Component Analysis (PCA) was used for identifying the common sources possible of chemical elements (Table 3 and Table 4). During summer season, we have observed three components which make up 71.36% of total variance of the studied elements. Therefore, the first principal component (PC 1), contains: conductivity, chlorine (Cl⁻), Magnesium (Mg²⁺), sulfate (SO₄⁻) and calcium (Ca²⁺), and it presents 39.23% of the total variance. The second principal component (PC2) contains: potassium (K⁺), sodium (Na⁺) and Bicarbonate (HCO₃⁻) with 17.22% of the total variance. And finally, the last component (PC3) contains: the organic matter, Nitrate (NO₃) and pH with 14.9% of the total variance (Table 3).

Tables 3a,b & 4: the Constituent of each component and the summary of each component: summer and winter

 Table 3a Rotated Component Matrix^{a*}
 Table 3b Rotated Component Matrix^{b*}

Table 4 Summary of Components	Table 4	Summary	of Com	ponents
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		Component	
	1	2	3
Cond	.973		
CI.	.938		
SO ₄	.896		
Mg ²⁺	.875		
Ca2 ⁺	.844		
\mathbf{K}^+		.880	
Na ⁺		.703	
HCO ₃		.587	
MO			.744
NO ₃			.698
pH			651

		Component		
	1	2	3	4
Cond	.969			
Mg ²⁺	.930			
Cl.	.923			
SO ₄	.631			
Ca ²⁺	.613			
\mathbf{K}^{+}		.796		
NO ₃		775		
Na^+		.620		
pН			860	
HCO ₃			.781	
MO				.95

Summer	season	winter	Season
	Variabl e (%)		Variable (%)
PC1	39.23	PC1	32.30
PC2	17.22	PC2	17.26
PC3	14.90	PC3	16.88
Cumul	71.36	PC4	10.69
ative		Cumul ative	77.13

a* Summer season, and

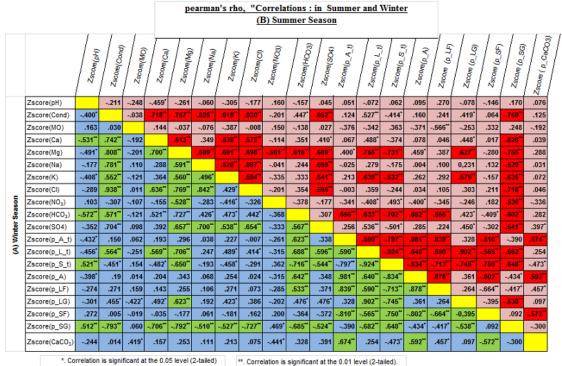
b* winter season

Extraction Method. Principal Component Analysis & Rotation Method. Varimax with Kaiser Normalization

In winter season, we have observed four components that make up 77.13% of total variance of the elements studied. The 1st principal component (PC1) are containing the conductivity, Chlorine (Cl⁻), sulfate (SO₄⁻), Magnesium (Mg²⁺) and Calcium (Ca²⁺), and it presents 32.23% of the total variance. PC2 Contains Potassium (K⁺), Sodium (Na⁺) and nitrates (NO₃) with 17.26% of the total variance; while PC3 contains bicarbonates (HCO₃-) and the pH with 16.86% of the total variance. The last component, PC4 is constituted by the organic matter with 10.69% of the total variance (Table 3).

In this study, it has shown that the elements grouped into PC1 (winter and summer), come from the common source. Indeed, the source of these elements is in the soil, as it was reported by the authors [31, 32]. We also find that the elements of the PC2: Na⁺ and K⁺ are always together and can also come from the soil. As well as for nitrates, they take origin in agricultural fertilizers (manure, chemical fertilizer) and generally go into groundwater by rain infiltration[32]. The organic matter in the winter classed in PC4 in his own group, it is more likely to come from the decomposition of plant or animal as well as the rainwater intake [33].

 Table 5: Correlation between physicochemical parameters and structure of soils



There is a higher significant correlation between physicochemical parameters during winter season than during summer season (Table 5). Indeed, for targeting only the significant points, the HCO₃, is statistically significant correlated during winter with pH (p = -0.611, Sig. < 0.05) (inverse correlation), conductivity (p = 0.505, Sig < 0.05), and Ca²⁺ (p = 0.512, Sig < 0.05) which is not the case during summer season.

The correlation coefficient between HCO₃ and SO₄ decreases from winter season to the summer season, with p = 0.571, sig < 0.01 for winter and p = 0.399, sig < 0.05 for summer. In case of HCO₃ and Mg²⁺, according season, there is no significant difference (p = 0.656 in winter, Sig. < 0.01 and p = 0.615 in summer, Sig. < 0.01), which indicates that, probably they come from a common source.

After analyzing the results, it have been shown that the cations: Calcium (Ca +), Magnesium (Mg +), sodium (Na +) and anions: Bicarbonate (HCO 3) Sulfates (SO4), Chlorine (Cl) do not show a fairly significant change according season variations (summer and winter) in the El Aarjate zone. This is confirmed by both Piper diagrams (Fig. 11), which show that in the cations' triangle, there isn't a dominant cation element. However, the anions' triangle shows a tendency to be much more in chlorinate for two seasons. As for the diagram which includes all ions, it shows that the groundwater of El Aarjate zone have been presented by two types of dominant facies, the first shown is bicarbonate calcium and magnesium, while the second is the chlorinated and sulfated of calcium and magnesium.

Therefore, the aquifer water properties in El Aarjate zone depend on the chemical characteristics of rock formations in which they circulate. Indeed, as the authors had mentioned [14, 19, 32], the change in the content of each element in groundwater depends on the type of soil which crossed, such as the permeable hydrogeological geochemical compositions allow exchanges with its tank. Therefore, the water-rock interaction is what eventually leads to change in the chemical characteristic of these waters [3, 22].

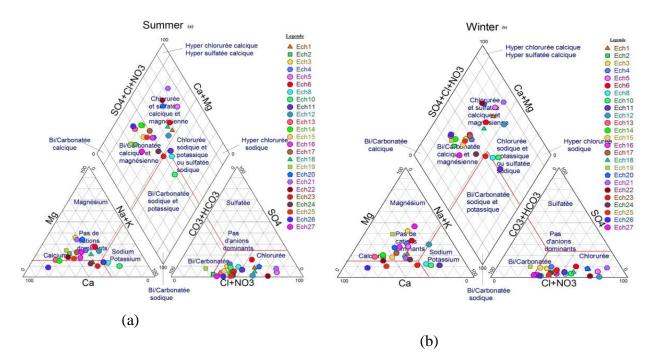


Figure 11. Piper Diagrams (a) summer and (b) winter

Conclusion

The results of this study have shown that some values of physicochemical parameters were below the limits on all sampled wells, and in most of the cases for others, are exceeding. Considering the number of locations with exceeding values reported and their spatial distribution, it can be concluded that are mainly local events, but need to be included into a future monitoring program. The concentrations of these parameters increasing depend of the use of chemical products in agriculture. The affirmation is supported by the results obtained in the three areas in correlation with the intensity and type of agriculture performed: Bab El Had area has the lowest rate of thresholds exceeding and the agricultural activities performed are based mainly on natural fertilizers, while on the other two areas the chemical fertilizers are used by most of the farmers.

Considering seasonal variation of the values measured for physicochemical parameters, it can be concluded that during rainy season (winter) the quality of ground water is decreasing, the incidence of WHO thresholds exceeding being increased for Conductivity, HCO3, NO3 etc...

The research, as a preliminary assessment of the El Aarjate zone area confirmed a low degree of contamination of the ground water. Although, this pollution is not alarming, therefore, it is important to constantly monitor water quality in this region and to inform people on the health risk that contamination could cause.

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