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Characterization and evaluation of the factors affecting the geochemistry of surface water of Koudiat Medouar Basin, Algeria

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Hydrochemistry of surface water in Koudiat Medouar Basin, Algeria was used to assess the quality of surface water for determining its suitability for drinking and agricultural purposes. In the three stations, there is a good correlation between the electrical conductivity and elements Ca, Mg, K, Cl, SO₄ and HCO₃. In order to determine the geochemical nature of water, the data was interpreted using the Piper diagram wherein the results show the predominance of Ca-Mg-HCO₃ or Ca-Mg-HCO₃-Cl water type in the Oued Reboa, Ca-Mg-HCO₃ or Ca-Mg-Cl-HCO₃ water type in the Oued Timgad and Ca-Mg-Cl-HCO₃ water type in the Reservoir dam. Principal components analysis results revealed that surface water quality was mainly controlled by geology, agricultural uses and domestic discharges. All the surface water samples in Oued Timgad fall in the field of C3S1, indicating high salinity and low sodium. Most of the surface water samples in Oued Reboa and in the reservoir dam fall in the field of C2S1, indicating medium salinity and low sodium. Based on RSC values, all the samples of the three stations had values less than 1.25 and were safe for irrigation.

Key words: Surface water, principal component analysis, drinking and irrigation water quality, Koudiat Medouar Basin, Algeria.

INTRODUCTION

In the current world economic paradigms, sustainable socioeconomic development of every community depends much on the sustainability of the available water resources. Water of adequate quantity and quality is required to meet growing household, industrial and agricultural needs. Surface water quality is a very sensitive issue, which transcends national boundaries. It is influenced by many factors, including atmospheric chemistry, the underlying geology, the vegetation (or organic matter decay), and anthropogenic agents. The solubility of minerals in water places an upper limit on the maximum amounts of certain species of chemicals in natural waters. Some minerals like carbonates and evaporites dissolve quickly and change the composition of water faster, while other minerals like silicates dissolve more slowly and have less conspicuous effects on the

composition of water. Temperature also plays a vital role in controlling the chemical and biological composition of a freshwater body. Previous studies (Frape et al., 1984; Garrels and McKenzie, 1967; Hem, 1989; Hartman et al., 2005) have revealed that the chemistry of natural waters can often be traced to the reaction of these waters with sediments or rocks through which they flow. Based on catchments studies in the USA, Walling (1980) observed differences in the weathering mechanisms of different rocks. Walling (1980) concluded that total dissolved solids in the water from limestones, volcanics and sand and gravel is almost independent of the amount of runoff. These differences in behavior accrue from the differences in the solubilities of the minerals present in these rocks. Since ultrabasic rocks are rich in pyroxenes and olivine, the predominant element expected from these rocks in freshwater is Mg. Similarly, Ca is the dominant cationic contribution from calcareous soils, and when Ca and Mg are present in about the same concentrations in a water body, they are probably derived

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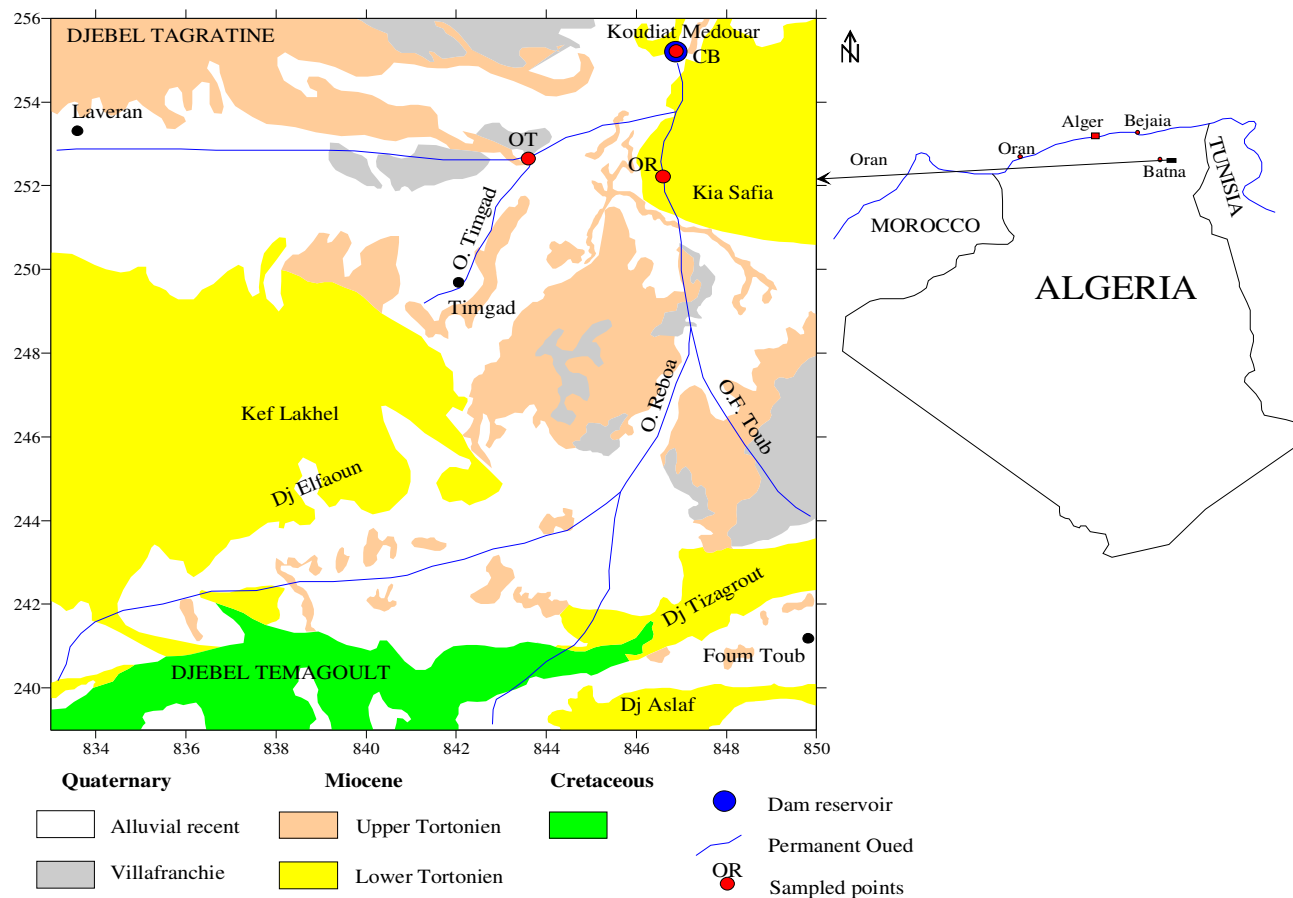


Figure 1. Map of the hydrographic network and drawing points.

from dolomite ($\text{CaMg}(\text{CO}_3)_2$). Atmospheric chemistry is the main source of Cl in freshwater bodies.

Organic matter decay can contribute phosphates, bicarbonate, nitrate, ammonia and dissolved solids to the chemistry of surface waters. Organic matter decomposition also has the tendency to reduce the dissolved oxygen (DO) content of natural water. Factors such as the residence time of water, the temperature and the presence of other ions play important roles in determining how much organic matter decays. Anthropogenic forces have the immense tendency to accelerate natural processes that affect water quality. Surface mining, mineral leaching and the uncontrolled use of toxics in industry can adversely affect the suitability of surface water resources for many purposes. Where chemical fertilizers are used in agriculture, nitrate and ammonia levels in surface waters have the tendency to rise to unacceptable levels. Many of the factors that influence water quality vary on spatial and temporal scales. A complete assessment of the role of these factors would require the consideration of both scales in the analysis.

The specific objectives of this study are: (1) Preliminary investigation and interpretation of the surface water quality of Koudiat Medouar basin; (2) Apply principal

component analysis to assess the main controls on the chemistry, and (3) find out the suitability of surface water for irrigation and drinking purposes.

Study area

The Koudiat Medouar watershed is located northeast of the city of Batna in the eastern part of Algeria (Figure 1). It has an area of 590 km² and controlled by a dam bearing the same name with a capacity of 62 millions cubic meters. The flow goes south to north and supplied by storms or by sewage disposal of bordering cities and villages. The average interannual precipitations are about 370 mm while the average annual temperature is around 15°. In the southern part of the area, limestone and malicious calcareon formations of the cretaceous crop out where the Miocene and the Pliocene, not distinguished, occupy the central part. It concerns the alternation of ferruginous red and gypseous clay which alternated with fine to course sandstone occupying an area of nearly 50 km². A conglomeratic marly and limestone serie, with limited extension, is added to this assemblage. The quaternary is represented by sheets of

Table 1. Surface water quality parameters.

Parameter	Method used
Chloride (as Cl in mg/L)	Argentometric titration
Carbonate (as CO ₃ in mg/L)	Titrimetry
Bicarbonate (as HCO ₃ in mg/L)	Titrimetry
Magnesium (as Mg in mg/l) EDTA	Titration
Calcium (as Ca in mg/L) EDTA	Titration
Sodium (as Na in mg/L)	Flame photometric method
Potassium (as K in mg/L)	Flame photometric method
Sulphate (as SO ₄ in mg/L)	Spectrophotometric method
Nitrate (as NO ₃ in mg/L)	Spectrophotometric method

screens of limestone or gritty origin, from recent alluvial deposits, and by limestone crust which crops out in many places (Vila, 1980; Wildi, 1983).

MATERIALS AND METHODS

Water samples

The 15 days control of the water of this watershed was realized at three stations: Oued Reboa, Oued Timgad, and in the dam reservoir. Samples were collected in good quality polyethylene bottles of 1 L capacity. Sampling was carried out directly without adding any preservatives in clean bottles to avoid any contamination and brought to the laboratory. Monitoring was done for 42 samples (from June 2004 to February, 2005). Only high pure chemicals (AnalR Grade) and double distilled water were used for preparing solutions for analysis.

Physical parameters like pH and EC were determined at the site with the help of digital portable water analyzer kit (Model No.: CENTURY-CK-710), and measured *in situ*. Determination of major cations and anions were realized in the laboratory using the analytical methods shown in Table 1 (Rodier, 1996). All the results are compared with standard limits recommended by World Health Organization (WHO, 1993).

Principal components analysis (PCA)

As a multivariate data analytic technique, PCA reduces a large number of variables (measured physical parameters, major anions and cations in water samples) to a small number of variables which are the principal components (PCs) (Qian et al., 1994). More concisely, PCA combines two or more correlated variables into one variable. This approach has been used to extract related variables and infer the processes that control water chemistry (Helena et al., 2000; Hidalgo and Cruz-Sanjulian, 2001).

Varimax rotation is applied to the PCs in order to find factors that can be more easily explained in terms of hydrochemical or anthropogenic processes (Helena et al., 2000). This rotation is called Varimax because the goal is to maximize the variance (variability) of the "new" variable, while minimizing the variance around the new variable (StatSoft Inc., 1997). The number of PCs extracted (to explain the underlying data structure) is defined by using the "Kaiser Criterion" (Kaiser, 1960) where only the PCs with eigenvalues greater than unity are retained. In other words, unless a PC extracts at least as much information as the equivalent of one

original variable, it is dropped (StatSoft Inc., 1997); however, for an in-depth account of the theory, refer to the work of Davis (1986).

RESULTS AND DISCUSSION

Chemistry of surface water

The analytical results of the chemical analysis and the statistical parameters of the three stations Oued Reboa, Oued Timgad and dam reservoir are presented in Table 2. The surface water samples of the study area have pH values ranging from 6.7 to 7.9, which indicate that the water is slightly alkaline. The electrical conductivity (EC) values ranged 510 to 1,534 $\mu\text{S}/\text{cm}$ in the three stations.

The mean concentration of magnesium varied from 61.42 to 154.4 mg/L (Table 2). All water samples exceeded the desirable limit of Mg for drinking water (50 mg/L) (WHO, 1993). The calcium value fluctuated between 73.74 and 168.33 mg/L (Table 2). The desirable limit of calcium for drinking water is defined as a proportion of 75 mg/L (WHO, 1993). We notice that all water surface samples of the three drawing points have exceeded the limit allowed by WHO. The sodium and potassium values are respectively 35.7 to 162.8 and 9.5 to 99.3 mg/L; all the studied samples exhibit sodium values less than those prescribed by WHO.

The content of bicarbonate varies from 97.6 to 646.4 mg/L where the mean value is 284.32 mg/l. It was noticed that the chloride, the sulfate and the nitrate contents values are respectively 14.2 to 184.6 and 68 to 18.6 mg/L, 0.2 to 3.6 mg/L and are below the standards prescribed by WHO.

Correlation coefficient is a commonly used measure to establish the relation between independent and dependent variables (Nair et al., 2005). The correlation matrix of 10 quality parameters, for the 42 samples, is indicated in Table 3. In Oued Reboa (OR) there is a good correlation between the conductivity EC and K, Cl, SO₄. Identically for Oued Timgad (OT) there is a strong correlation between EC and HCO₃. However in the dam

Table 2. Summary statistics of the analytical data.

	Oued Reboa					Oued Timgad					Dam Reservoir				
	Min	Max	Mean	SD	C _v	Min	Max	Mean	SD	C _v	Min	Max	Mean	SD	C _v
EC	510	752	643	94	15	848	1534	1252	218	17	575	784	682	74	11
pH	7.1	7.7	7.6	0.2	2.4	6.8	7.9	7.4	0.3	4.2	6.8	7.9	7.5	0.2	3.3
Ca	78.55	120.90	100.01	11.90	11.90	89.77	168.33	117.08	22.59	19.29	73.74	100.20	86.66	8.30	9.57
Mg	72.35	103.90	91.23	9.04	9.91	77.57	154.49	105.23	21.89	20.80	61.42	92.80	79.18	8.81	11.12
Na	70.30	80.00	74.57	3.22	4.32	115.00	162.80	134.97	15.00	11.12	35.70	108.80	52.39	23.12	44.13
K	13.13	39.60	25.50	7.07	27.72	12.31	99.30	65.59	22.33	34.05	9.50	39.60	26.07	8.78	33.66
Cl	14.20	42.60	31.08	9.34	30.06	71.00	184.60	118.35	31.08	26.26	17.75	31.95	22.40	4.22	18.84
SO ₄	71.00	184.40	157.91	31.89	20.19	68.80	186.00	160.14	37.68	23.53	69.00	149.90	119.79	22.75	18.99
HCO ₃	225.30	373.30	267.74	44.59	16.65	213.50	646.60	442.26	149.25	33.75	97.60	189.10	142.97	25.41	17.77
NO ₃	0.50	2.60	1.18	0.62	52.53	0.20	3.60	1.29	1.14	87.95	0.20	0.80	0.48	0.16	33.97

All values are in mg/l except pH and EC ($\mu\text{S}/\text{cm}$).

Table 3. Correlation matrix.

	EC	Ca	Mg	Na	K	Cl	SO ₄	HCO ₃
Oued Reboa								
EC	1							
Ca	0.398	1						
Mg	0.454	0.923	1					
Na	-0.002	-0.348	-0.310	1				
K	0.738	0.528	0.507	-0.237	1			
Cl	0.673	0.739	0.810	-0.435	0.600	1		
SO ₄	0.622	0.816	0.888	-0.464	0.666	0.804	1	
HCO ₃	0.386	0.586	0.663	0.332	0.389	0.316	0.503	1
Oued Timgad								
EC	1							
Ca	-0.530	1						
Mg	-0.586	0.914	1					
Na	-0.187	0.313	0.393	1				
K	0.442	0.033	0.221	0.425	1			
Cl	-0.280	0.703	0.743	0.529	0.432	1		
SO ₄	0.307	0.129	0.364	0.468	0.867	0.528	1	
HCO ₃	0.551	-0.309	-0.384	-0.307	-0.125	-0.445	0.068	1
Dam reservoir								
EC	1							
Ca	0.911	1						
Mg	0.881	0.946	1					
Na	-0.563	-0.413	-0.283	1				
K	0.375	0.201	0.165	-0.723	1			
Cl	0.435	0.163	0.133	-0.227	0.159	1		
SO ₄	0.790	0.720	0.656	-0.850	0.553	0.086	1	
HCO ₃	0.787	0.938	0.870	-0.237	0.152	0.121	0.530	1

reservoir (CB), a good correlation is observed between the EC and elements Ca, Mg, SO₄ and HCO₃.

Major cations and anions such as Ca, Mg, Na, K, HCO₃, SO₄ and Cl in meq/L were plotted in Piper's tri

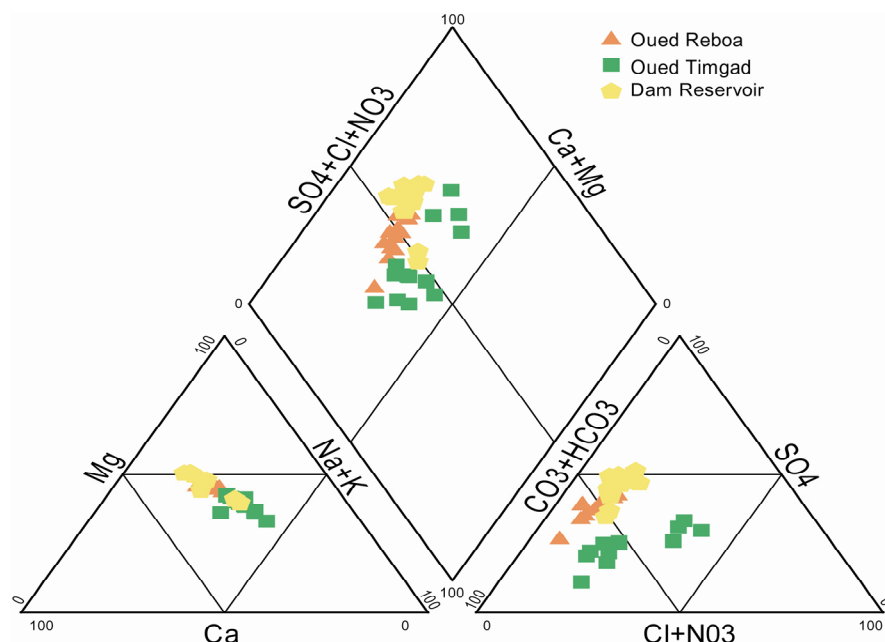


Figure 2. Piper diagram representing hydrochemical facies.

Table 4. Principal component weights

	Oued Reboa		Oued Timgad		Dam Reservoir		
	PC1	PC2	PC1	PC2	PC1	PC2	PC3
EC	0.71	-0.23	-0.47	-0.80	0.96	-0.08	-0.19
Ca	0.89	0.03	0.80	0.35	0.93	-0.34	0.06
Mg	0.92	-0.03	0.90	0.21	0.88	-0.41	0.06
Na	-0.36	-0.90	0.66	-0.25	-0.67	-0.68	-0.09
K	0.76	-0.05	0.45	-0.83	0.48	0.74	0.10
Cl	0.89	0.20	0.90	-0.10	0.29	0.16	-0.94
SO ₄	0.95	0.12	0.53	-0.79	0.87	0.30	0.24
HCO ₃	0.60	-0.70	-0.55	-0.35	0.83	-0.45	0.05
Eigen values	4.88	1.41	3.70	2.31	4.79	1.62	1.00
Variance (%)	61.03	17.58	46.24	28.82	59.83	20.19	12.55
Cummulative (%)	61.03	78.62	46.24	75.06	59.83	80.03	92.57

linear diagram (Piper, 1944) to evaluate the hydrochemistry of surface water of Koudiat Medouar basin (Figure 2). The following facies are indicated: Ca-Mg-HCO₃ and Ca-Mg-HCO₃-Cl water type (Oued Reboa). Ca-Mg-HCO₃ and Ca-Mg-Cl-HCO₃ water type (Oued Timgad). Ca-Mg-Cl-HCO₃ water type (dam reservoir).

On the basis of Walton's classification (Walton, 1970), nearly 73% of the water samples showed excess of acid with respect to strong acid.

Principal components analysis

Principal components analysis (PCA) was used to reduce

alkaline earth with respect to alkalis at the three drawing points, and nearly 80% of the surface water samples showed an excess of weak acid with respect to strong acid in Oued Timgad, and nearly 75% of the surface water samples showed an excess of strong acid with respect to weak acid in the dam reservoir whereas in Oued Reboa, all samples showed an excess of weak

the number of variables and to identify the most important variables by separating the groups, in fact extracting the factors that control the chemical variability. In this analysis, the axes (principal components) may represent the dominant underlying processes and should help to constrain any process-based models of hydrochemical

Table 5 surface water quality parameters for irrigation purposes

	Oued Reboa				Oued Timgad				Dam Reservoir			
	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
SAR	1.151	1.567	1.305	0.108	1.82	2.772	2.201	0.271	0.63	2.149	0.989	0.467
Na%	20.606	27.904	23.898	1.982	29.206	43.672	34.522	4.527	14.849	33.902	21.302	5.409
RSC	-10.040	-6.170	-8.109	1.013	-15.410	-2.370	-7.252	4.394	-9.540	-6.890	-8.497	0.769

evolution. In this situation, we anticipate that the chemistry of surface water is derived from typical water-sol-rock interaction. In addition, there may be contributions from anthropogenic sources that can produce distinct chemical differences compared to natural background. This technique can highlight those outliers or groups of samples that are controlled by such factors from the more persuasive natural background. Detailed analysis showed that two and three PCs are the most meaningful choice for the system.

For the Oued Reboa dataset, two significant PCs explain 78.62% of the variance of the original dataset (Table 4). Most of the variance is contained in the PC1 (61.03%), which is associated with the variables EC, Ca, Mg, K, Cl and SO₄ (Table 4). This component reflects the signatures of water-soil-rock interaction. PC2 explains 17.58% of the variance and is mainly related with the Na and HCO₃. The HCO₃ can be the result of the dissolution of carbonate minerals.

For the Oued Timgad dataset, two PCs explain 75.06% of the variance (Table 4). Most of the variance is contained in the PC1 (46.24%), which is associated with the variables Ca, Mg, Na, Cl and HCO₃. PC1 includes classical hydrochemical variables originating from weathering processes. PC2 explains 28.82% of the variance and is related with the EC, K and SO₄. As Oued Timgad is surrounded by traditional farm lands, an agricultural source of SO₄ is possible. Use of copper sulfate (CuSO₄) is very widespread practice in the agricultural activities of the area. Copper sulfate is a fungicide used to control bacterial and fungal diseases of fruit, vegetable, and field crops. It is used in combination with lime and water as a protective fungicide, referred to as Bordeaux mixture (Taha, 2002). For the dam reservoir dataset, three significant PCs explain 92.57% of the total variance (Table 4). PC1 of the reservoir dam which explains 59.83% of the total variance has high loadings in that EC, Ca, Mg, SO₄, and HCO₃ ions and probably shows the result of mineral water reactions in the area. PC2, which explains 20.19% of the total variance, includes Na and K. PC3, has a high loading of Cl and explains 12.55% of the total variance. Based on geological and geographical position, industrial discharges and contamination of the surface water by seepage were excluded as source of high concentrations. A local contamination by waste water, sewage systems, agricultural fertilizers, draining and the dissolution of the clay, marl

formations could be responsible for this increase.

Irrigation water quality

Sodium adsorption ratio (SAR) is an important parameter for determining the suitability of surface water for irrigation because it is a measure of alkali/sodium hazard to crops. SAR is defined by (Richards, 1954; Karanth, 1987)

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

where the concentrations are reported in meq/L.

The SAR range from 0.63 to 2.77 meq/L (Table 5); all samples fall in low sodium class (Table 6). The analytical data obtained by the salinity diagram (Wilcox, 1948) illustrates that all the surface water samples in Oued Timgad fall in the field of C3S1, indicating high salinity and low sodium water, which can be used for irrigation on almost all types of soils with little danger of exchangeable sodium (Figure 3). Most of the surface water samples (95%) in Oued Reboa and in the dam reservoir fall in the field of C2S1, indicating medium salinity and low sodium in the water.

All sampling points are found suitable with respect to EC for irrigation purposes. According to Wilcox classification (Wilcox, 1955), the water surface in the study area is ranging between excellent to good for irrigation uses (Table 6). The primary effect of high EC reduces the osmotic activity of plants and thus interferes with the absorption of water and nutrients from the soil.

The sodium percentage (Na %) is calculated using the formula given below:

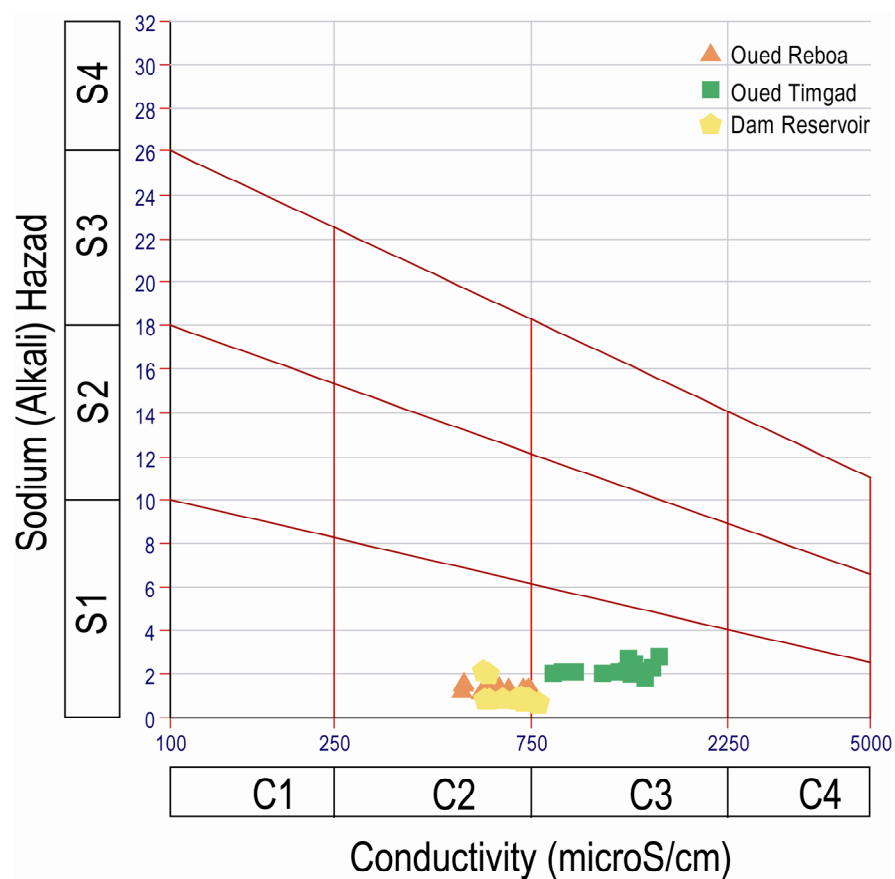
$$\text{Na} = [(\text{Na} + \text{K}) * 100] / [\text{Ca} + \text{Mg} + \text{Na} + \text{K}] \quad (2)$$

where all the concentrations are expressed in meq/L.

The values of sodium percent are varying from 27.90 to 43.67% (Table 5). Most of the sampling stations falling under the good category while one sample falls in permissible category and four samples fall in excellent category (Table 6). When the concentration of sodium ion is high in irrigation water, Na tends to be absorbed by clay particles, displacing magnesium and calcium ions. This exchange process of sodium in water for Ca and Mg

Table 6. Classification of surface water on the basis of Na %, SAR, EC and RSC.

Parameters	Range	Water class	Samples
Na %	20	Excellent	CB _{11, 12, 13, 14}
	20-40	Good	OR-OT-CB _{1, 2, 3, 4, 5, 6, 7, 8, 9, 10}
	40-60	Permissible	OT ₁₀
	60-80	Doubtful	Nil
	80	Unsuitable	Nil
SAR	10	Excellent	All
	18	Good	Nil
	18-26	Doubtful	Nil
	26	Unsuitable	Nil
EC	250	Excellent	Nil
	250-750	Good	OR-CB _{1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12}
	750-2000	Permissible	OT-CB _{13, 14}
	2000-3000	Doubtful	Nil
	3000	Unsuitable	Nil
RSC	< 1.25	Safe	OR-OT-CB
	1.25-2.5	Moderate	Nil
	> 2.5	Unsuitable	Nil

**Figure 3.** Water classification according to EC and SAR values.

in soil reduces the permeability and eventually results in soil with poor internal draining.

In waters having high concentration of bicarbonate, there is a tendency for calcium and magnesium to precipitate as the water in the soil becomes more concentrated. As a result, the relative proportion of sodium in the water is increased in the form of sodium carbonate. Residual sodium carbonate (RSC) is calculated using the following Equation 3.

$$\text{RSC} = (\text{CO}_3 + \text{HCO}_3) - (\text{Ca} + \text{Mg}) \quad (3)$$

where all ionic concentrations are expressed in meq/L.

According to the US Department of Agriculture, water having more than 2.5 of RSC is not suitable for irrigation purposes. Surface water of the study area was classified on the basis of RSC and the results are presented in Tables 5 to 6 for the three stations. Based on RSC values, all the samples of the three stations had values less than 1.25 and were safe for irrigation.

Conclusion

Interpretation of hydrochemical analysis reveals that the surface water in Koudiat Medouar basin is moderately hard, fresh to slightly saline and slightly alkaline in nature. Piper diagram characterizes the water types. Oued components analysis results revealed that surface water Reboa was found to be of Ca-Mg-HCO₃ and Ca-Mg-HCO₃-Cl type whereas in the Oued Timgad, there is a shift to Ca-Mg-HCO₃, Ca-Mg-Cl-HCO₃ type and in the dam Reservoir is Ca-Mg-Cl-HCO₃ type. Principal quality was mainly controlled by geology, agricultural uses and domestic discharges. The values of sodium absorption ratio and electrical conductivity of the surface water were plotted on the US salinity laboratory diagram for irrigation water. All the surface water samples in Oued Timgad fall in the field of C3S1, indicating high salinity and low sodium. Most of the surface water samples in Oued Reboa and in the reservoir dam fall in the field of C2S1, indicating medium salinity and low sodium. Based on RSC values, all the samples of the three stations had values less than 1.25 and were safe for irrigation.

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