

HYDROGEOCHEMICAL PROCESSES AND SUITABILITY ASSESSMENT OF SURFACE WATER IN THE GROUZ DAM BASIN, NORTHEAST ALGERIA

M. Lalaoui¹, Z. Allia², M. Chebbah^{1,*}

¹LSNM, SNV department, university A.Boussouf of Mila, BP 26 RP 43000 Mila, Algeria

²LSNM, ST department, university A.Boussouf of Mila, BP 26 RP 43000 Mila, Algeria

Received: 22 June 2020 / Accepted: 31 August 2020 / Published online: 01 September 2020

ABSTRACT

Surface water is the principal source of water for domestic use and agricultural irrigation in Grouz Dam Basin and adjacent regions. This research aims to evaluate hydrochemical characteristics and suitability for domestic and agricultural irrigation purposes of the Grouz Dam Basin surface waters. The surface waters were categorized as alkaline hard freshwater and are classified into Na-Cl and mixed water types. The values of measured parameters are below the maximum allowable limits for drinking except for Na^+ , NO_3^{2-} and turbidity. Dissolution and anthropogenic activity are the dominant hydrogeochemical processes controlled surface water chemistry. Overall, it was found that surface waters are unsuitable for drinking by cons they are suitable for irrigation. The results of this study will be useful in regional surface water management and protection.

Keywords: Grouz Dam, Surface water, Hydrochemistry, Quality, Suitability assessment, Algeria.

Author Correspondence, e-mail: m.chebbah@centre-univ-mila.dz

doi: <http://dx.doi.org/10.4314/jfas.v12i3.29>



1. INTRODUCTION

In southern countries like Algeria, water quality becomes increasingly critical following an excessive exploitation often uncontrolled due to an increase in demand. However, as water quality is determined by its composition and it is affected by various natural or anthropogenic parameters [1,2], its Hydrogeochemical characteristics can reflect several influences, including lithology of watersheds and reservoirs, climate, atmospheric inputs and human activities. Thus, it is important to determine the hydrochemical characteristics of water and its possible controls for its assessment and sustainable utilization [3]. The hydrochemical evaluation of water systems are usually based on the availability of a large amount of information concerning water chemistry [4]. To manage water resources effectively, it is important to understand the geochemical evolution of water in its environment, as this information can improve the knowledge of hydrochemical systems. In the upstream Kebir sub-basin, NE Algeria, surface water is the most momentous resource for people's lives, irrigation and industry. Its waters, stored and regulated by the Grouz Dam reservoir, are principally intended to supply drinking water a part of Constantine city and to irrigate around 5000 hectares of agricultural land in the region. So, the surface water resource assessments and sustainability considerations become of utmost importance in this area. However, in recent years, a few water quality assessment research projects were done in this region [5,6]. In this paper, for the first time, the surface water quality in the basin was assessed to will enhance the understanding of hydrogeochemical processes, and the protection and sustainable utilization of surface water resources. It provides a theoretical basis to policymakers in Algeria for developing suitable water resource exploitation strategies and policies for this region in this new century in full of crises and changes. So, the main objective of this study was hydrochemical assessment and evaluation of suitability water quality for various uses in the upstream Kebir sub-basin. It is mainly focused to: (1) evaluate surface water quality in the study area based on the detailed hydrogeochemical analysis of physicochemical parameters; (2) determine hydrogeochemical characteristics of the surface water, and consequently understand and identify the parameters controlling the solubility of major elements in such semi-arid region; (3) study the feasibility of surface water usage for various purposes

(domestic and irrigation purposes). This, in order to provide a basis for the scientific assessment of water use and conservation and for future studies on the hydrochemical processes and their evolution in the study area.

2. MATERIALS AND METHODS

2.1 The Study area

The Kebir Upstream sub-basin, High Plateaus domain, is located in northeastern Algeria between the Tellian domain in the North and the Hodnean domain in the South (**Figure 1**). It forms the southern part of the largest Kebir-Rhumel hydrographic basin of Algeria that corresponds to the upper Rhumel river valley and located at about 35 Km South-west of Constantine and 30 km South of Mila city between latitudes $36^{\circ} 08' N$ and $36^{\circ} 15' N$ and longitudes $6^{\circ} 10' E$ and $6^{\circ} 18' E$, encompassing an area of about 1130 km^2 (**Fig. 1**). It is an almost circular basin, closed downstream by the eastern end of Djebel Grouz, drained by the Rhumel Wadi which flows only thanks to the precipitation, temporary flow of West-East direction, and controlled by the Hammam Grouz Dam (capacity: 45000 m^3 , regularizing volume: 9550 m^3) at Oued Athménia [7].

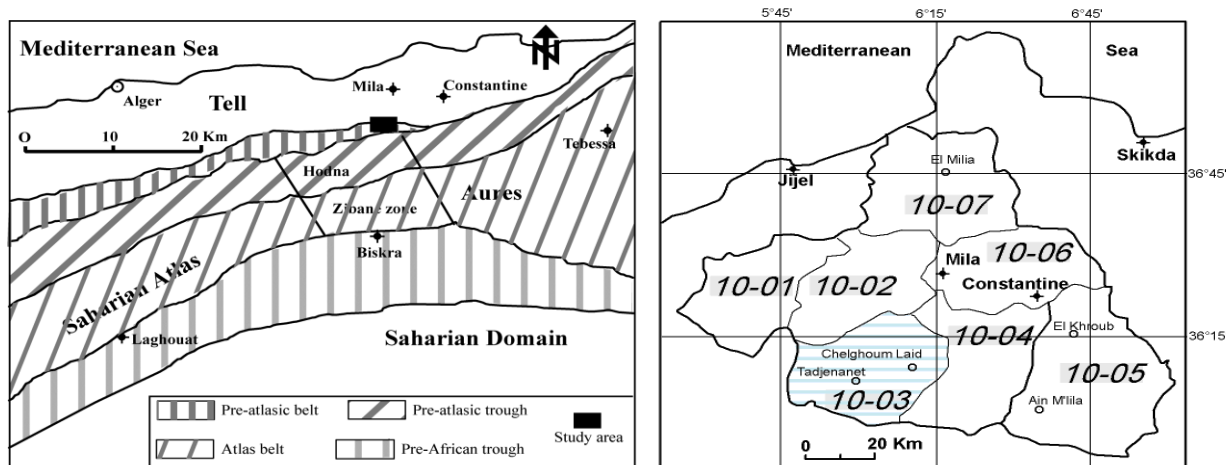


Fig.1. A. Major geomorphologic units of North Algeria

B. Kebir Rhumel subbasins (10-01: O. Dehamcha- kebir upstream, 10-02: O. Kebir upstream - Endja, 10-03: O. Kebir upstream, 10-04: O. Rhumel – Seguen, 10-05: O. Boumerzoug, 10-06: O. Rhumel – Smendou, 10-07: O. Maritime Kebir)

This sub-basin is a Mio-Plio-Quaternary plain surrounded by isolated and abrupt reliefs

representing the neritic limestone massifs and windows of Dj. Sattor and Djemila thrust sheets [8] and is subject to a semi-arid climate (**Fig. 2**). Precipitation occurs irregularly, and the rainy season extends from October to May. The average rainfalls are around 390.50 mm/year and mean annual temperatures are around 16.10 °C.

The geology of the region is characterized by three litho-stratigraphic sets [9]: a Lower Jurassic-Cretaceous neritic carbonate complex, covered by a dominant marly group from Upper Senonian to Paleocene, and an upper set comprising heterogeneous detrital Mio-Plio-Quaternary series (**Fig. 2**). The plain is filled by the Mio-Plio-Quaternary alluvial deposits; they are essentially claying with limestone, marl, silt, sandstone and conglomerate banks, always limited in thickness and extent, with rapid facies changes. The clays, in certain places contain numerous blocks, gravel or debris flow. The soil is generally alluvial fine rather favorable to agriculture (cereals and vegetable crops) and industrial activity revolves mainly around the agglomeration of Chelghoum Laid (over 46 000 inhabitants) with its detergent factory [10].

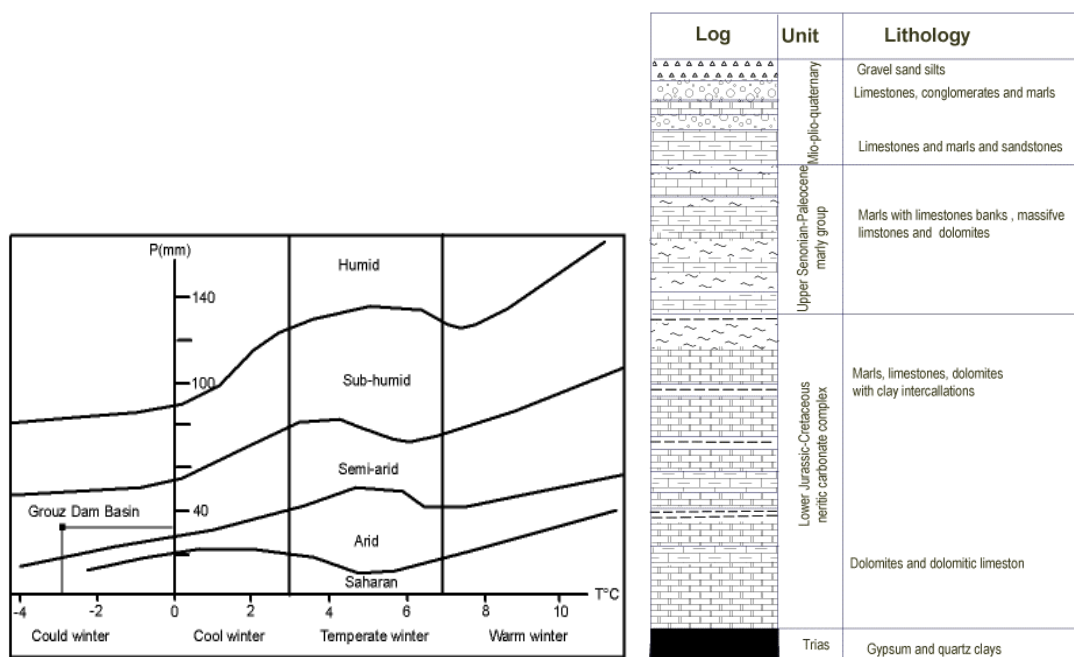


Fig.2. Emberger climagram and lithostratigraphic log in Grouz dam Basin

2.2 Sampling and analytical methods

To assess the surface water hydrogeochemistry in the study area, a total of representative 27 water samples were collected (15 samples from river, 12 samples from lake; **Fig. 3**) in

January 2020. Standard methods [11] were used during the collection and analysis of the samples. For each sampling point, two replicate water samples were collected in 1.5-L dry, clean, and sterilized plastic bottles. The sampling bottles were rinsed with the water to be collected, and the samples were filled till the rim. One of the bottles was acidified with HNO_3 for cation determination, and another was kept unacidified for the anion analyses. The collected samples were transferred on the same day to the laboratory for the chemical analysis and were stored below 4°C . For all samples, temperature, pH, electrical conductivity (EC), total dissolved solids (TDS), and salinity were determined in the field itself with standard field equipment, using portable devices (multi parameter sensodirect 150). The major (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , CO_3^{2-} , HCO_3^- , SO_4^{2-} , Cl^- and NO_3^{2-}) and minor (PO_4^{3-} , P, Fe, Al, Cu, and Mn) ions were analyzed in the laboratory of Natural Sciences and Materials (LSNM), University of Mila using ion photometers (Palintest photometer 7500 and Lovibond photometer MD600). Sodium was determined by using a flame photometer (Agilent 240/280 Series AA). Further, the ion balance error was also calculated to verify the accuracy of major ion analysis, and it was within acceptable limit of $\pm 5\%$ [12].

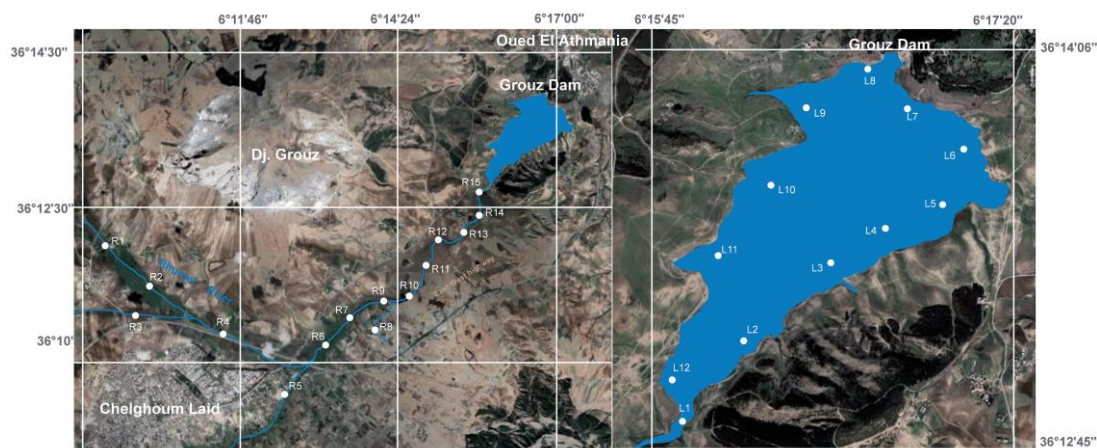


Fig.3. Location of samples (R1: River water samples, L1: Lake water samples)

3. RESULTS AND DISCUSSION

3.1. Surface water physicochemical characteristics

Enter Summary statistics of physicochemical parameters (minimum, maximum, mean and standard deviation of various parameters) of the surface water samples and guideline values of the World Health Organization [13] for drinking water are shown in **Table 1**.

Table 1. Summary statistics of physicochemical parameters of river and lake water samples with standards for drinking-water quality of WHO

	River				Lake				WHO (2008)	
	Mim	Max	Moy	SD	Mim	Max	Moy	SD	DL	MPL
pH	7,6	9,03	8,14	0,43	7,96	8,95	8,53	0,32	6.5-8.5	9.2
CE ($\mu\text{s.cm}^{-1}$)	865	2040	1281,9	366,4	144	1358	1029,6	301,7	900	1400
TDS (mg.l^{-1})	464	1090,0	682,47	196,28	522,0	747,0	593,25	65,87	600	900
Sal (mg.l^{-1})	400	1200	620	221,1	500	800	550,	100	-	-
TH (mg.l^{-1})	398	828	478,1	100,3	370	552	445,8	52,5	100	500
TA (mg.l^{-1})	252	519	323,4	67,0	238	296,0	263,33	19,04	-	-
Turb (NTU)	1,1	32,3	12,93	11,1	1,7	93,5	43,7	61,1	5	10
Ca (mg.l^{-1})	98	165	127,9	22,2	95	175	136,6	22,4	75	200
Mg (mg.l^{-1})	42,0	137,0	70,53	29,83	44,0	75,0	53,83	7,94	50	150
K (mg.l^{-1})	2,9	172,5	35,41	46,73	15,0	47,5	20,84	0,81	-	-
Na (mg.l^{-1})	162,0	272,1	238,47	35,27	242,0	259,15	257,73	4,95	-	200
Cl (mg.l^{-1})	360,0	460,0	398,93	27,61	380,0	420,0	400,00	0,00	250	600
SO₄ (mg.l^{-1})	126,0	284,0	184,53	41,27	190,0	300,0	206,67	30,10	200	500
CO₃ (mg.l^{-1})	28,0	100,0	46,80	16,47	10,0	56,0	37,67	13,88	125	350
HCO₃ (mg.l^{-1})	196,0	465,0	276,60	61,90	188,0	276,0	225,67	22,75	125	350
NO₃ (mg.l^{-1})	13,2	108,0	62,81	28,98	52,0	124,0	76,27	20,23	50	-
PO₄ (mg.l^{-1})	1,0	27,0	9,867	8,245	3,0	11,0	5,90	2,923	200	-
P (mg.l^{-1})	0,40	8,9	3,107	2,606	1,0	3,6	1,96	0,91	-	-
Fe ($\mu\text{g.l}^{-1}$)	50	450	170	117	140	9400	1047	2,64	300	-
Al ($\mu\text{g.l}^{-1}$)	-	110	24	29	-	860	180	235	200	-
Cu ($\mu\text{g.l}^{-1}$)	-	640	257	174	100	4800	1153	1275	2000	-
Mn ($\mu\text{g.l}^{-1}$)	2	8	3	2	4	24	7	5	400	-

Min: minimum, **Max:** maximum, **Moy:** mean, **SD:** standard deviation, **DL:** Desirable limits, **MPL:** Maximum

permissible limits. CE, TDS, Salinity, TH and TA Values are at 25°C

The pH ranges from 7.6 to 9.03 (mean: 8.14) in the river water, and the pH has a range of 7.96 to 8.95 (mean: 8.53) in the lake water. Only 80% and 50 % samples from rivers and lakes, respectively, show pH values in the permissible limit and indicating the alkaline nature. The alkalinity, as CaCO_3 , determined in the laboratory, ranges from 252 to 519 mg.l^{-1} (mean: 324.4) in river water, and from 238 to 296 mg.l^{-1} (mean: 263.3) in lake water. Most of the samples show relatively high alkalinity (250 mg.l^{-1}) however few samples (14.81%) show a medium alkalinity, but remains within acceptable limits. The electrical conductivity (EC) ranges from 865 to 2040 $\mu\text{S.cm}^{-1}$ (mean: 1281.86 $\mu\text{S.cm}^{-1}$) in river water and from 977 to 1358 $\mu\text{S.cm}^{-1}$ (mean: 1104.58 $\mu\text{S.cm}^{-1}$) in lake water.

The total dissolved solids (TDS) ranges from 464 to 1090 mg.l^{-1} (mean: 682.48 mg.l^{-1}) in river water, and from 522 to 747 mg.l^{-1} (mean: 593.25 mg.l^{-1}) in lake water. The most samples show TDS values below 1000 mg.l^{-1} and can be considered as fresh waters, however two tributaries samples (R3 and R8) are classified as brackish water according to the WHO guidelines. The total hardness in CaCO_3 ranges from 398 to 828 mg.l^{-1} (mean: 478.07 mg.l^{-1}) in the river water, and the total hardness has a range of 370 to 552 mg.l^{-1} (mean: 445.75 mg.l^{-1}) in the lake water indicating that all of these waters are very hard. The turbidity ranges from 1.11 to 32.30 NTU (mean: 12.93 NTU) in the river water and of 1.66 to 93.5 NTU (mean: 43.68 NTU) in the lake water. Among major cationic concentrations (mg.l^{-1}): calcium (Ca^{2+}) ranges from 98 to 165 (mean: 127.93) in river water and ranging from 95 to 175 (mean: 136.58) in lake water; magnesium (Mg^{2+}) ranges from 42 to 137 (mean: 70.53) in river water and ranging from 44 to 75 (mean: 53.85) in lake water; sodium (Na^+) ranges from 162 to 272 (mean: 238.47) in river water and ranging from 242 to 259 (mean: 257.73) in lake water; potassium (K^+) ranges from 2.9 to 172.5 (mean: 35.41) in river water and ranging from 15 to 47.5 (mean: 20.84) in lake water; All water samples fall within the acceptable limits for drinking water. Thus, the major cations are dominated by Na^+ and Ca^{2+} (via, $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$) in all water. Among the major anionic concentrations (mg.l^{-1}): Chloride (Cl^-) ranges from 360 to 460 (mean: 398.93) in river water and ranging from 400 to 400 (mean: 400) in lake water, a single sample exceeds the authorized limit of 250 mg.l^{-1} ; the carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) range respectively from 28; 196 to 100; 465 (mean: 46.8;

276.6) in river water and ranging from 10; 188 to 56; 276 (mean: 37.67; 256,67) in lake water; sulfate (SO_4^{2-}) ranges from 126 to 284 (mean: 184.53) in river water and ranging from 190 to 300 (mean: 206.67) in lake water, the majority of sampled waters does not exceed the permissible WHO guideline value of 250 mg.l^{-1} . Nitrate (NO_3^-) ranges from 13.2 to 108 (mean: 62.8) in river water and ranging from 52 to 124 (mean: 76.28) in lake water, the most samples exceed the permissible limit of 50 mg.l^{-1} . So the major anions of surface water are dominated by Cl^- and HCO_3^- (via, $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{CO}_3^{2-}$) in all waters (**Fig. 4**).

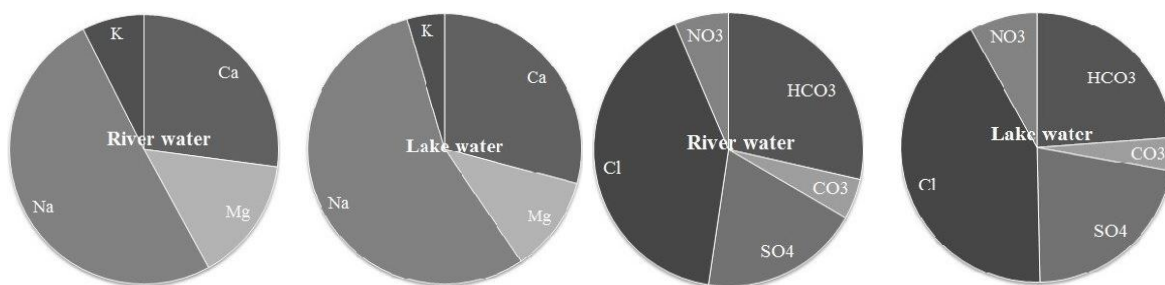


Fig.4. Pie diagram for major cations and anions of River water and Lake Water

3.2. Hydrochemical characteristics and process of the surface

3.2.1. Hydrochemical facies

Graphical representation of surface and groundwater major dissolved constituents (major cations and anions) helps in understanding its hydrochemical evolution, grouping and areal distribution. In the present study, Piper trilinear diagram and Durov diagram were constructed to evaluate variation and evolution in hydrochemical facies of studied waters. Water Quality Hydrochemistry diagrams (Diagrammes) version 6.6.1 and Grapher Software version 14 were used to plot these diagrams.

Piper trilinear diagram: The Piper trilinear diagram [14] is useful for geochemical evaluation, and it is a graphical presentation of the major ions to quickly determine the water hydrochemical facies. It is a multifaceted plot where in milliequivalent percentage concentrations of major cations and anions are plotted in two triangular fields, which were then projected further into the central diamond field thus determining the chemical facies of water. Ionic concentrations were plotted in a piper diagram to evaluate the geochemical features of the sampled surface water (**Fig. 5**); it shows the dispersion of all samples in the chloride water type field, except for one sample of river water (R8) which corresponds to

sample of small tributary. However, the all samples are concentrated in the sodium-potassium and non-dominant type fields for cations. The projection of the points in the central diamond-shape shows that majority of the samples belong to Na-K-Cl-SO₄ field signifying the dominance of alkali over alkaline earths ($\text{Na}^+ + \text{K}^+ > \text{Ca}^{2+} + \text{Mg}^{2+}$) and strong acidic anions over weak acidic anions. The remaining samples are plotted under Ca-Mg-Cl-SO₄ field demonstrating the dominance of alkaline earths over alkali ($\text{Ca}^{2+} + \text{Mg}^{2+} > \text{Na}^+ + \text{K}^+$) and strong acidic anions over weak acidic anions ($\text{Cl}^- + \text{SO}_4^{2-} > \text{HCO}_3^- + \text{CO}_3^{2-}$). This reveals the presence of two main type facies: sodium chloride type (53.33 % of river water, 75 % of lake water) and mixed type (46.67% of river water, 25 % of lake water).

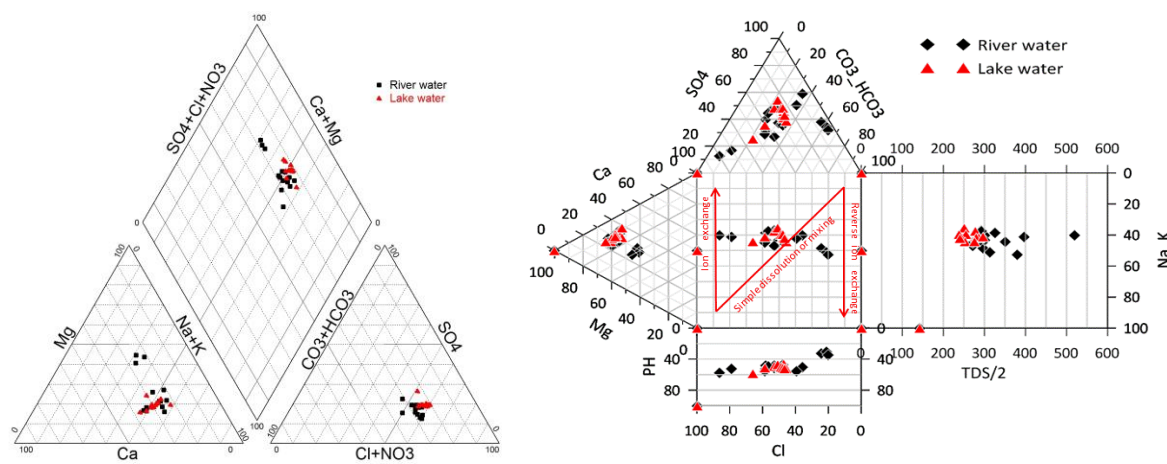


Fig.5. Piper Trilinear diagram classifying major hydrochemical facies and Durov plot depicting hydrochemical processes involved

Durov diagram: In addition to the Piper diagram an overall characterization of hydrochemical facies of the surface water was carried out by using Durov Diagram [15]; it is a composite plot consisting of two ternary diagrams where the cations of interest are plotted against the anions of interest; sides form a central rectangular, binary plot of total cation vs. total anion concentrations. The expanded version includes TDS (mg.l^{-1}) or pH data added to the sides of the binary plot to allow further comparisons. Where the intersection of lines extended from the points in ternary diagrams and projected on the sub-divisions of the binary plot of diagram define the hydrochemical processes involved along with water type. The main purpose of the Durov diagram [16] is to cluster the data points indicating the samples with

similar chemical composition as well as to reveal a useful relationships and properties for a large sample groups and define the hydrochemical processes involved along with water type. The hydrochemical data in the study area were plotted on a Durov diagram by using Grapher version 14 software (**Fig. 5**); the plot shows that the most sample plots fell in the field of Na-Cl with less representation in mixed Ca- Mg-Cl and Ca-Mg-SO₄ facies for lake water by against the samples of river water are scattered in the fields of Na-Cl and mixed Ca-Mg-Cl or Ca-Mg-SO₄ facies. Furthermore, the majority of samples plot along the dissolution or mixing line, except for a few samples of river water which are plotted above and below the equilibrium line indicating ion exchange. This trend can be attributed to fresh recent recharge water exhibiting simple dissolution or mixing with no dominant major anion or cation [17]. The anions and cations in surface water could come mainly from the weathering and dissolution of carbonate, sulphate and salt rocks, and could also be associated with anthropogenic activities [18,19].

3.2.2. Mechanism controlling geochemistry of surface water

The soluble ions of surface and groundwater can be sourced from a variety of geochemical processes occurring as water reacts with the geologic materials which it flows such as chemical weathering, precipitation, mixing and various anthropogenic factors. To clarify the materials and mechanisms involved in the water mineralization in the study area, several correlations were performed such as Gibbs, $(Ca^{2+} + Mg^{2+}) - (SO_4^{2-} + HCO_3^-)$, $Cl^- - (Na^+ + K^+) / Cl^-$ and $Cl^- - (Na^+ + K^+)$ diagrams or Ca / Mg ratio [19,20].

Gibbs diagram is used to distinguish the effects of these different processes and represents the relationship between lithological features of watershed or aquifers and surface or groundwater composition [21]. Gibbs plots (**Fig. 6**) show three distinct controlling mechanisms and sources of ionic components such as precipitation, evaporation dominance, and rock dominance. In the Gibbs (TDS versus $Na^+ / (Na^+ + Ca^{2+})$ and $Cl^- / (Cl^- + HCO_3^-)$) diagrams, the all samples are plotted in the field of rock weathering (**Fig. 6**), indicating water-rock interaction is the main factor controlling dissolved hydrochemical components of water samples. This indicates that the surface water of the study area is influenced by chemical weathering of rocks and minerals which regulates the ions species composition in surface

water favoured by atmospheric precipitation that is a diffusion source of pollution as they contain micro and macro-elements and influence water chemistry [22].

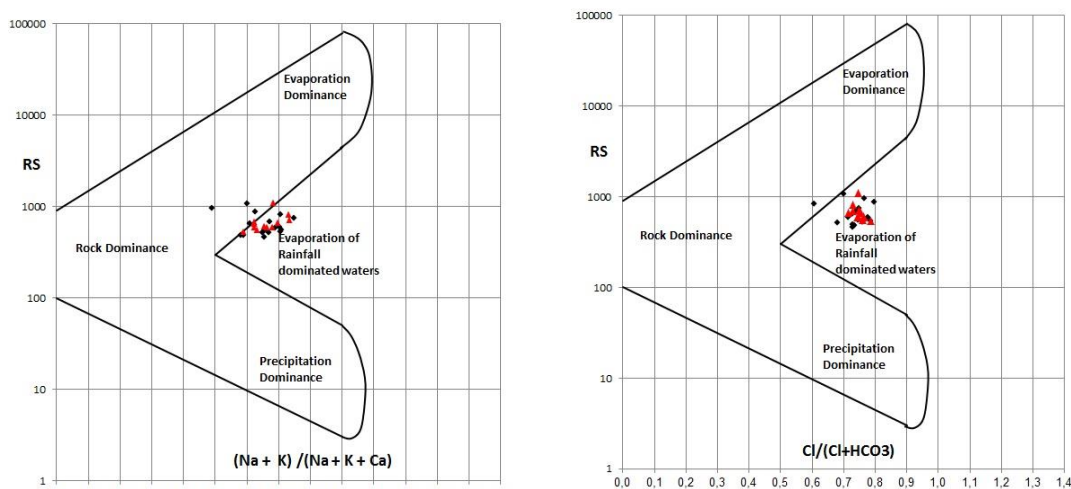


Fig.6. Mechanisms governing surface water chemistry in the study area (after Gibbs, 1970)

Sodium, calcium and magnesium are the dominant cations present in the surface water; similarly, chloride, carbonate, bicarbonate and sulphate are also present in important amounts. These major ions in natural waters come, principally, of weathering and dissolution of limestone, gypsum, salt, and partly silicate minerals. The ions from these sources might have been dissolved and added to the water system by leaching and mixing processes. However, mineral weathering and dissolution suggested a simple plot of $(Ca^{2+} + Mg^{2+})$ versus $(SO_4^{2-} + HCO_3^-)$ could provide information on the relative importance of the main minerals contributing to surface water mineralisation. In the $((Ca^{2+} + Mg^{2+})$ versus $(SO_4^{2-} + HCO_3^-))$ diagram, if Ca^{2+} , Mg^{2+} , SO_4^{2-} , and HCO_3^- are derived from simple dissolution of calcite, dolomite, and gypsum, then samples plot along the 1:1 equiline in this diagram. If the points shift to the right due to the excess of SO_4^{2-} and HCO_3^- contents, they reflect the presence of ion exchange [23,24]. In the case of presence of reverse ion exchange processes, the points shift to the left due to the excess of Ca^{2+} and Mg^{2+} ions [25, 24]. The plot of the $(Ca^{2+} + Mg^{2+})$ versus $(SO_4^{2-} + HCO_3^-)$ diagram diagram (**Fig. 7**), in the study area shows that the most samples take place around and above the equiline, tree (03) samples of river water plot above the 1:1 equiline. Plot of samples along and around the 1:1 equilibrium line indicates that source of Ca^{2+} , Mg^{2+} , SO_4^{2-} , and HCO_3^- ions are derived from simple dissolution of calcite, dolomite, and gypsum. The samples placed above equilibrium reflect the presence of reverse

ion exchange due to the excess of Ca^{2+} and Mg^{2+} ions.

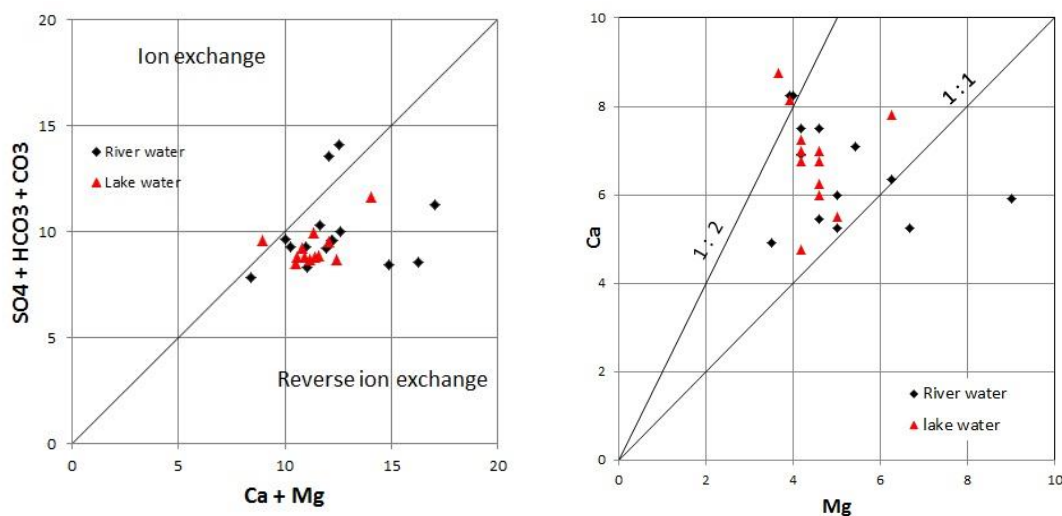


Fig.7. $(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-})$ and $\text{Ca}^{2+} - \text{Mg}^{2+}$ scatter diagrams for surface water in the study area

Moreover, the $\text{Ca}^{2+}/\text{Mg}^{2+}$ molar ratio is used to clarify the dissolution of carbonates [26]. If the ratio $\text{Ca}/\text{Mg} = 1$, the dolomite dissolution should occur, whereas a higher ratio is indicative of greater calcite contribution. Molar ratio of $\text{Ca}/\text{Mg} > 2$ indicates the dissolution of silicate minerals, which contribute calcium and magnesium to surface and groundwater and the most water samples have a ratio between 1 and 2, indicating the dissolution of calcite and dolomite [27]. The plot of Ca/Mg scatter diagram of the surface water samples of the study area reveals that the dominant process is the dissolution of carbonates (**Fig. 7**). The most samples plotted between lines 1 and 2 ($\text{Ca}/\text{Mg} > 1$) and below 1:1 line ($\text{Ca}/\text{Mg} = 1$) indicate the calcite and dolomite weathering prominent process. However, samples lie above the 1: 2 line ($\text{Ca}/\text{Mg} > 2$) indicating the effect of silicate minerals. The presence of carbonates and mineral silicates in the sediments favors the weathering process.

Furthermore, if only carbonate dissolution occurs, the values of $\text{Ca}^{2+}/\text{HCO}_3^-$ and $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ will be close to 0.5. In the study area, the values of $\text{Ca}^{2+}/\text{HCO}_3^-$ and $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ were higher than 0.5 (**Fig. 8**), which suggests that the excess Ca^{2+} and Mg^{2+} were not only the result of carbonate dissolution but were also influenced by other natural sources, e.g., gypsum and the silicate mineral [28]. Similarly, if the Ca^{2+} originates from gypsum dissolution, the ratio of $\text{Ca}^{2+}/\text{SO}_4^{2-}$ will be nearly equal to 1 [29]. However, in this

study, the ratio of Ca^{2+}/SO_4^{2-} is much greater than 1 (**Fig.8**), suggesting that the excess Ca^{2+} may be derived from the dissolution of carbonates and in small proportion from silicate minerals. Also, the $(Na^+ + K^+) - Cl^-$ relationship has often been used to identify the mechanisms to acquire salinity in semi-arid / arid regions. In general, evaporation causes an increase in concentrations of all ions in water. If evaporation process is dominant and no minerals species are precipitated, the $(Na^+ + K^+)/Cl^-$ ratio is unchanged [29].

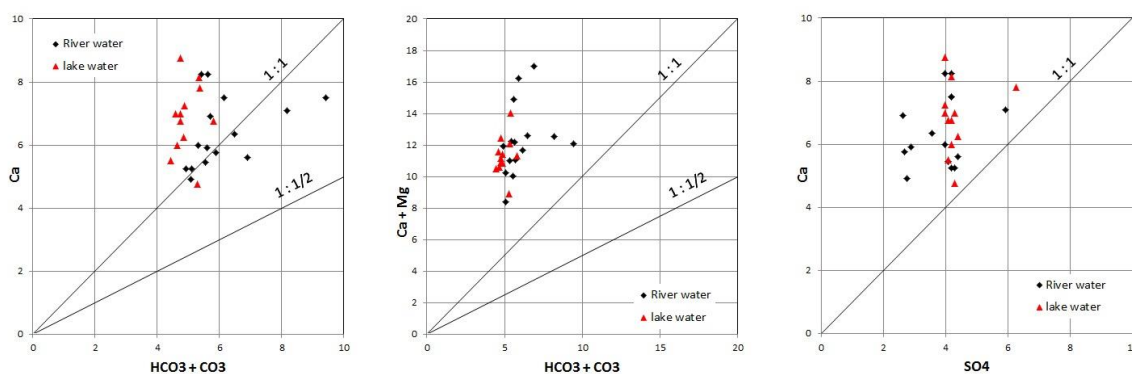


Fig.8. $(HCO_3^- + CO_3^{2-}) - Ca^{2+}$, $(HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+})$ and $SO_4^{2-} - Ca^{2+}$ scatter diagrams for surface water in the study area

Hence, the plot $(Na^+ + K^+)/Cl^-$ versus Cl^- would give a horizontal line, which would indicate concentration by evaporation and transpiration (**Fig. 8**). If the Na^+ and K^+ in water samples come from salts dissolution, then the ratio of $(Na^+ + K^+)/Cl^-$ is around 1, whereas a ratio >1 is interpreted that Na^+ and K^+ are released from a silicate weathering reaction [30].

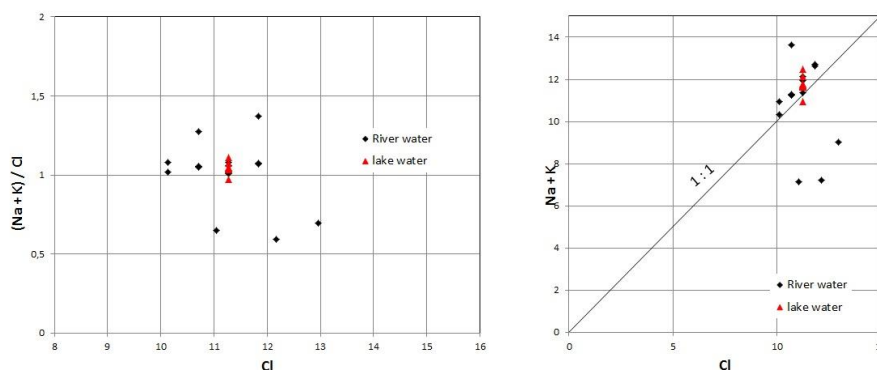


Fig.9. $Cl^- - (Na^+ + K^+)/Cl^-$ and $Cl^- - Na^+ + K^+$ scatter diagrams for surface water in study area

In the study area, the $(Na^+ + K^+)/Cl^-$ ratio ranges from 0.59 to 1.37 with an average of 1.02. When $Na^+ + K^+$ is plotted against Cl^- (**Fig. 9**), most of the samples that lie around the 1: 1

trend line indicating salt dissolution (halite and sylvite). The samples that lie below the 1: 1 line show excess Cl^- , emphasizing that the deficit $\text{Na}^+ + \text{K}^+$ comes from silicate weathering due to feldspar weathering by reverse ion exchange process.

3.3. Suitability of surface water

3.3.1. Suitability of surface water for drinking

The adequacy of surface water for domestic use is directly related to different physiochemical parameters and their concentrations. The drinking water status in the study area was evaluated by comparing with the specification of TDS, TH, EC, Turb, Na^+ , Cl^- , SO_4^{2-} , NO_3^{2-} , PO_4^{3-} , P and metallic traces set by the World Health Organization (WHO) [22]. The analytical results of physical and chemical parameters of surface water were compared with the standard guideline values recommended by WHO the for drinking and public health purposes (**Table 1**, **Table 2**). The concentrations of ions, such as Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-} are below the maximum allowable limits for drinking, by against, 92.6 % of samples exceed the maximum allowable limits for Na^+ . The NO_3^{2-} concentration varies from 13.2 to 124 mg.l^{-1} .

Table 2 Classification of samples according specified for drinking water quality parameters

	Range	Class	N° of samples	% of samples
EC	< 250	Excellent	0	0
	250-750	Good	0	0
	750-2000	Permissible	26	96.30
	> 2000	Doubtful	1	3.70
TDS	< 300	Excellent	0	0
	300 -600	Good	14	51.85
	600-900	Fair	11	40.74
	900-1200	Poor	2	7.41
	> 1200	Unacceptable		
TH	< 75	Soft	0	0
	75-150	Moderately hard	0	0
	150-300	Hard	0	0
	>300	Very Hard	27	100
Turb	< 2	Excellent	2	7.41
	2-5	Good	5	18.52
	5-10	Permissible	2	7.41
	10-15	Doubtful	2	7.41
	>15	unsuitable	16	59.26

CE: Electrical Conductivity, TDS: total dissolved solids, TH: Total Hardness, Turb: Turbidity.

Only 18.52 % of river water samples have a nitrate level not exceeding the maximum permissible limit for drinking water (50 mg.l^{-1}); therefore the surface waters are unsuitable for drinking and public health purposes. The phosphate and phosphor (PO_4^{3-} , P) concentrations range from 1.4 to 35.9 mg.l^{-1} (mean: 9.75) and are very below the maximum allowable limits for drinking. The metallic trace contents (Fe, Al, Cu, Mn) of surface water samples were determined for water quality in study area (**Table 1**). The maximum contents of Fe, Al, Cu and Mn water samples were determined as 9400, 860, 4800, and $24 \text{ }\mu\text{g.l}^{-1}$, respectively. The Fe, Al, Cu and Mn contents in the water samples are within the permissible limit of WHO for 78.78%, 92.6%, 92.6 % and 100% of the total analyzed samples respectively. The TDS content of the surface water in most water samples (92.6 %) is less than 900 mg.l^{-1} and 7.4% is less than 1200 mg.l^{-1} in all water samples (**Table 2**). The EC content of the surface water in most water samples (96.3 %) is less than the maximum allowable limits for drinking ($2000 \text{ }\mu\text{s.cm}^{-1}$) (**Table 2**). Therefore, the TDS and CE contents are considered satisfactory, and surface water can be used for drinking without any risk, with respects to this two parameters. The TDS - TH plot (**Fig. 10**) shows that most surface water samples in these watersheds are hard-fresh water. Two water samples (R3 and R8) with high TDS ($>1000 \text{ mg.l}^{-1}$) and TH ($>400 \text{ mg.l}^{-1}$) values are classified as very hard-brackish water. TH of water is caused primarily by the presence of cations such as calcium and magnesium and anions such as carbonate, bicarbonate but has no known adverse effects. In water samples, hardness values range from 370 to 828 mg.l^{-1} with an average value of 463.7 mg.l^{-1} and belongs to the very hard water category. Surface water exceeding the limit of 300 mg.l^{-1} of CaCO_3 is considered very hard [31]. Per the WHO international standards, 500 mg.l^{-1} is the TH maximum permissible limit for drinking water and, 100 mg.l^{-1} the most desirable limit. 7.4 % of samples (R3 and L7) exceed the maximum allowable limits (**Table 2**). If reference is made to pH, all surface water samples are permissible for drinking water, where only 33.33 % of the water samples (20% river water, 50% lake water) exceed the desirable limits for drinking. In water samples, Turbidity values range from 1.11 to 234 NTU with an average value of 34.4 NTU. 50 % of river water and 91.66 % of lake water samples exceed the maximum allowable limits (10 NTU) and therefore this water can not be used for domestic purposes in their raw states.

The surface water in the study area is unsuitable for drinking and domestic uses based, principally, on the concentrations of nitrates and quality parameters like turbidity. In these regions, surface water is polluted by urban discharges and human activities.

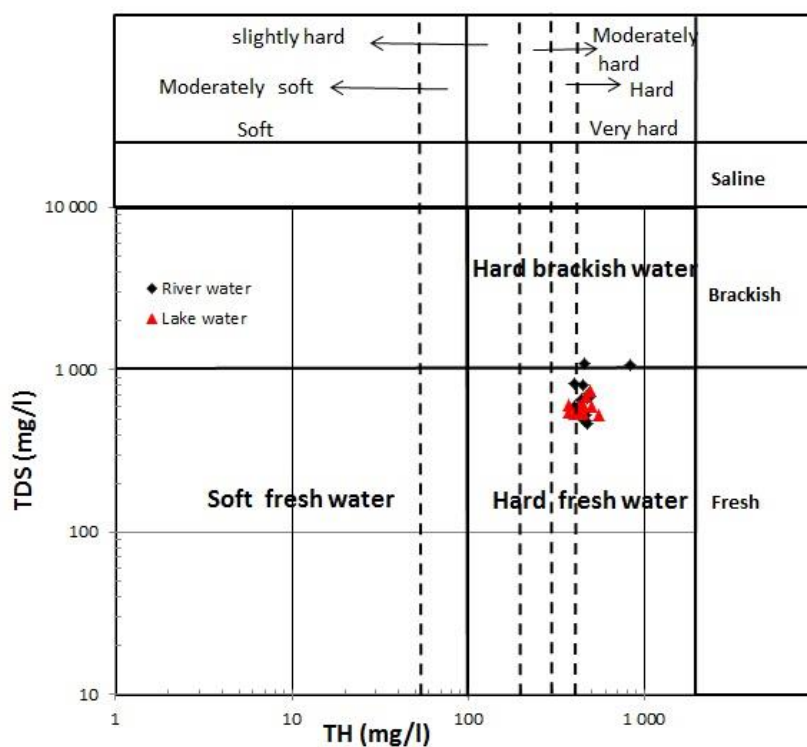


Fig.10. Surface water quality for drinking purposes in the study area

3.3.2. Suitability of surface water for irrigation

The development and maintenance of successful irrigation projects involve not only the supplying of irrigation water to the land but also the control of salt and alkali in the soil is as important as the supplying of irrigation water for the development and maintenance of successful irrigation projects [32]. The suitability of surface water for irrigation is conditional on the effects of mineral constituents of water on both the plant and soil. Excessive amount of dissolved ions in irrigation water affects plants and agricultural soil physically and chemically, thus reducing the productivity. Agriculture and related labor are the main occupation of the rural people in the Grouz dam basin. Therefore, the determination of irrigation water quality in the region is gaining importance. Salinity, electrical conductivity, and indexes such as sodium absorption ratio (SAR), sodium percentage (%Na), and residual sodium carbonate (RSC) are critical factors used for determining the suitability of water resources for

agricultural applications [33,34].

Sodium Adsorption Ratio (SAR)

The SAR is the effective parameter used for ascertaining the suitability of surface and groundwater for irrigation purposes because it is a measure of alkali/ sodium hazard to crops. Salinity and toxicity problems of irrigation water are attributed to SAR. High Na⁺ concentration in water may deteriorate the physical structure of the soil essentially by displacement of exchangeable cations Ca²⁺ and Mg²⁺ from the clay minerals of the soil and such soil becomes impermeable leading to low fertility and cultivation ability [35,36].

The SAR was calculated by the following equation given by USSL [37] as:

$$SAR = Na / \sqrt{(Ca + Mg) / 2} \quad \text{where, all ions are expressed in meq.l}^{-1}.$$

The SAR values of water samples in the study area ranged from 2.50 to 5.37 with an average value of 4.47. Salinity classification was done using a USSL quality diagram (**Fig. 11**). The diagram has 16 classes, with reference to SAR as an index of sodium hazard and EC as an index of salinity hazard. By plotting the obtained results in the diagram (**Fig. 11**), 77.6 % of surface water samples fall in the field of C3–S1, highlighting high salinity and low sodium in surface waters, which is suitable for the irrigation of all soil types with little danger of exchangeable sodium. However, 22.4 % of samples fall in C3–S2 field, reflecting medium alkalinity hazard and high salinity of surface water. This may indicate that irrigation water can come from the referred surface waters little danger of exchangeable sodium on all types of soils. These low to medium SAR and high salinity suggest that the studied surface waters are suitable to moderately suitable for irrigation purposes without any threat of imposition of any hazard.

Percent sodium (Na %)

The percent sodium is an efficient parameter in differentiating water because high value is the indication of soft water whereas a low value signifies hard water, also the soluble sodium is important in categorizing irrigation water in terms of soil permeability because sodium has profound effect on soil permeability and soil structure thereby results in little or no plant growth [40]. A high Na⁺ concentration in irrigation water will result in negative influences on soil structure resulting in poor internal drainage and restricted circulation of air and water

when Na^+ is displaced by mg^{2+} and Ca^{2+} and is adsorbed by clay soil particles [41]. Na % is computed by the following equation:

$$\text{Na \%} = \frac{\text{Na} + \text{K}}{\text{Ca} + \text{Mg} + \text{Na} + \text{K}} \times 100 \quad \text{where the concentrations are in } \text{meq.l}^{-1}.$$

The plot of analytical data on the Wilcox diagram shows that 85.2 % of surface water samples belong to good to permissible category and 14.8% falls in the field of permissible to doubtful category (Fig. 11).

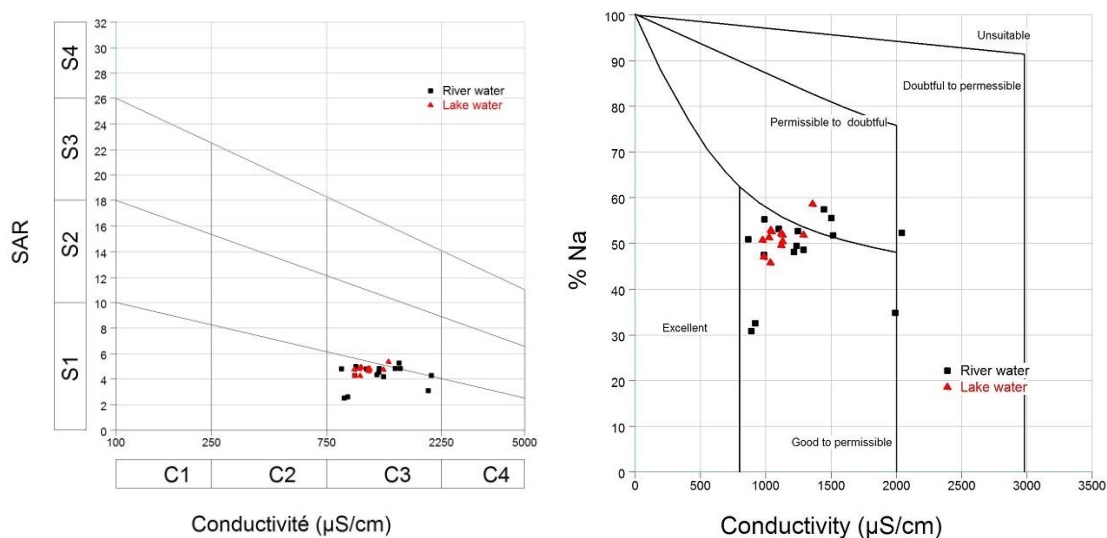


Fig.11. Diagram for irrigation waters classification plot of percent sodium vs electrical conductivity [38] and Classification of irrigation water on the basis of Wilcos diagram [39] plotted between SAR versus EC value for evaluating alkalinity and salinity hazard

Residual Sodium Carbonate (RSC)

The RSC index of water/soil signifies the alkalinity hazard posed by it and finds the suitability of water for irrigation [42] and is calculated to determine the hazardous effect of carbonate and bicarbonate ions on the quality of water for agricultural purposes.

RSC is defined by the equation:

$$\text{RSC} = (\text{HCO}_3^- + \text{CO}_3^{2-}) - (\text{Ca}^{2+} + \text{Mg}^{2+}), \text{ where all concentrations are expressed in } \text{meq.l}^{-1}.$$

The classification of irrigation water according to RSC values is waters containing more than 2.5 meq.l^{-1} of RSC are not suitable for irrigation practices, while those having 1.25 – 2.5 meq.l^{-1} are doubtful and those with less than 1.25 meq.l^{-1} are good for irrigation. Hence in the

present study where RSC values range between -10.36 and -2.66, all samples have RSC <1.25; it can be concluded that water in this area belong to the good category and without poses any alkaline hazard to the soil.

4. CONCLUSIONS AND RECOMMENDATIONS

The surface water hydrochemistry and quality in study area has been evaluated for their chemical composition and suitability for various uses. The results of this investigation provide an outline of the geochemical processes controlling surface water chemistry and then surface water quality in the study area. Results of physicochemical parameters were compared with the standard guideline values recommended by WHO for drinking and public health purposes and suggest that all water samples are hard freshwaters and alkaline in nature. The concentrations of ions, such as Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and PO_4^{3-} are below the maximum allowable limits for drinking, by against, 92.6 % of samples exceed the maximum allowable limits for Na^+ . Most surface water samples have a nitrate level exceeding the maximum permissible limit (50mg.l^{-1}) indicating that those waters are unsuitable for drinking and public health purposes. The metallic traces (Fe, Al, Cu and Mn) contents in water samples are within the permissible limit for 78.78%, 92.6%, 92.6 % and 100% respectively. The turbidity values of the most water samples exceed the maximum allowable limits (10 NTU) and therefore this water can not be used for domestic purposes in their raw states. The relative concentrations of major cations and anions occur in the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{Cl}^- > (\text{HCO}_3^- + \text{CO}_3^{2-}) > \text{SO}_4^{2-} > \text{NO}_3^-$ respectively and surface waters are Na-CL and mixed water types. Surface water chemistry in the study area was mainly controlled by rock weathering and originates from the dissolution of carbonate, sulphate and salt, as well as cation reverse exchange, in addition to anthropogenic actions. The conjugated action of different mineralisation processes as well as their combinations had accentuated the salinity of these waters. Their identification allowed a better interrelationship among the different present ions. The surface water is unsuitable for drinking and domestic uses based, principally, on nitrate concentrations and quality parameters like turbidity. In this region, surface water is polluted by urban discharges and human activities. However, irrigation assessment using SAR, % Na and RSC indicated that the surface waters were within good to permissible irrigation water

class with low salinity hazard and are suitable for most crops on most soils; there was neither salinity nor toxicity problem of irrigation water, and hence the surface water can safely be used for long-term irrigation. The results of hydrochemistry detailed evaluation reported in this paper will provide a basis for assessment, management, and water use in Kebir upstream sub-basin. They will help to design regional-scale studies of surface-water quality and to find out appropriate remediation techniques minimizing elevated levels of anthropic occurring contaminants. This will, firstly, reduce water treatment costs of Grouz Dam destined for drinking and secondly to preserve this precious resource in this region. As surface water contamination within the basin constitutes a serious threat for human welfare and the natural environment. Accordingly, promoting a sustainable monitoring and management of surface water resources and implementing measures to aid people and farmers in adopting the appropriate management practices are of high priority and should contribute in mitigating water quality problems and ensuring surface water sustainability. In addition, a regular water quality monitoring and multidisciplinary water research programs also facilitate the sustainable surface water management on this semi-arid region of Algeria.

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How to cite this article:

Lalaoui M, Allia Z, Chebbah M. Hydrochemical processes and suitability assessment of surface water in the Grouz Dam Basin, Northeast Algeria. J. Fundam. Appl. Sci., 2020, 12 (3), 1452-1474.