Geochemical Analysis of Soil Facies and Groundwater Quality in the Valley of Oued Righ in Southern Algeria, with a Specific Focus on the Terminal Complex

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Abstract

Groundwater plays a crucial role in arid regions like the Oued Righ valley, where high evaporation rates make it the primary water resource. This study aims to evaluate the quality of the Complex Terminal groundwater in the Oued Righ region. Various analyses, including temperature, electrical conductivity (E.C), pH, total dissolved solids (TDS), and ion concentrations (such as Ca^{2+}, Mg^{2+}, Cl^{-}, HCO_3^{-}, SO_4^{-2}, NO_3^{-}, NO_2^{-}, PO_4^{-3}, Iron, and Fluor), were conducted to determine the chemical water facies, their interactions, and suitability for human consumption and agricultural use. The results reveal that the Complex Terminal aquifer exhibits a neutral pH (7.33 ± 0,2) and moderate mineralization (TDS = 2395.25 ± 771.18 mg/l). However, some parameters indicate pollution and undesirability, such as nitrite, iron, and fluorine, exceeding the World Health Organization's standards. On the other hand, ions like nitrate and orthophosphate meet the recommended standards. The groundwater in the Complex Terminal aquifer undergoes water-rock interactions, forming impermeable geochemical facies primarily composed of clay, gypsum, and anhydrite (Bel and Demargne., 1966). This mineralization is attributed to the correlation between calcium and sulfate ions, originating from the alteration of anhydrite, a calcium sulfate compound. This work focuses on investigating the relationship between irrigation water and soil salinity through the direct measurement of neutral salts in the soil's imbibition water (Omran and Marwa, 2015). The accumulation of neutral salts in soils is influenced by the intensity of irrigation, and their toxicity can harm plants while reducing water availability. High concentrations of Cl^- can particularly affect plant tissues and leaves. The hydrogeochemical properties of the study area are primarily influenced by the interaction between water and rock, as well as cation exchange (Cornet, 1964). Soil acidity, measured by pH, was found to be moderately acidic in most samples (ranging from 7.4 to 7.8), except for the southern part of the study area, which exhibited alkalinity in the Goug and Baldet Omar areas. The Oued Righ region is characterized by the accumulation of NaCl, which can be attributed to the presence of chloride ions and sodium cations, showing strong correlations of 0.95 and 0.94, respectively. These factors directly impact the electrical conductivity and the presence of other salts, thus influencing their variation.

Keywords: Mineralization, geochemical facies, pollution, groundwater, irrigation, arid zones.

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1. Introduction

Groundwater plays a paramount role in many parts of the world, particularly in areas with arid climates. The Oued Righ Valley, which harbors the most abundant watercourse in the Lower Algerian Sahara, has transformed into a significant drainage system. It functions as an entirely artificial river resulting from the seepage of wastewater from oases and settlements (Moulla and Guendouz, 2003).

The study area experiences a hyperactive climate, indicating that the available water reserve is depleted throughout the year, leading to an annual agricultural deficit. Consequently, the exploitation of underground aquifers has become the sole water resource in the Oued Righ Valley. Since the first drilling operation in 1856, the number of boreholes has rapidly increased over time to meet the demands of agricultural irrigation, as well as industrial and domestic consumption. However, this resource is currently facing contamination threats from various sources (Ravikumar et al., 2011).

The objective of this study was to assess the water quality of the Terminal Complex, elucidate the mechanisms underlying the mineralization of these water reserves, and examine their hydrochemistry, geochemical facies, and the origin of groundwater mineralization (Bel and Cuche, 1970). To achieve this, the interrelationships among physico-chemical parameters (Ramdani et al., 2016), pollution parameters, undesirable parameters, and overall mineralization parameters were analyzed using statistical methods (Karakus and Yıldız, 2019).

2. Framework of the study

The sand dunes, salts and artesian waters (Halassa et al 1968) recognize the Lower Sahara (Fig.1). It is bounded to the north by the Saharan Atlas, to the east by the reverse of the Tuniso-Libyan Dahar, to the west by the ridge of the M'Zab, and to the south by the highlands of Tademait and Tinghert.

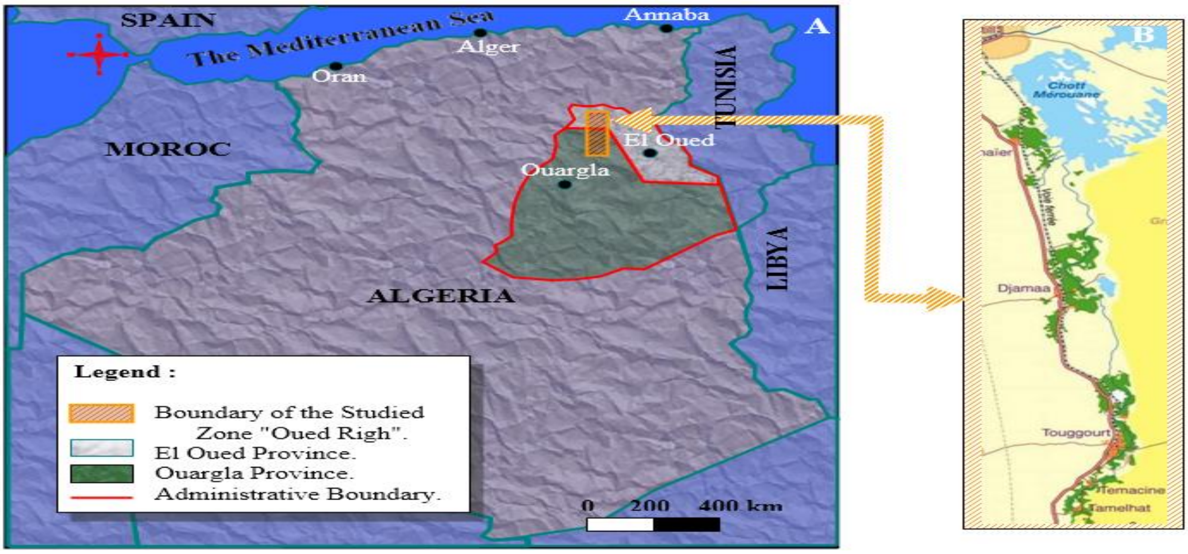


Fig. 1. (A) Geographical location of the study areas, and (B) the map of Oued Righ

The region of Oued Righ is part of the Lower, Sahara and marked essentially by a linear depression of north-south orientation with a length of 125 km, marked by palm groves of which the most important from the south to the north (from "upstream" to "downstream") are: El-Goug, Blidet-Amor, Tamellaht, Temacine, Touggourt, Moggar, Tamerna, Djamaa, Ourlanha, M'Ghaier, Ourir, and Oum El-Thiour.

2.1 Hydrogeology

The Complex Terminal or Subsurface of this study is generally shallow, varying between 100 and 400 m, with a low temperature (Bouselsal and Belksier, 2018), (Chaib et al., 2013). Its chemical composition is good at the edges and average in the center of the basin (Fig. 2).

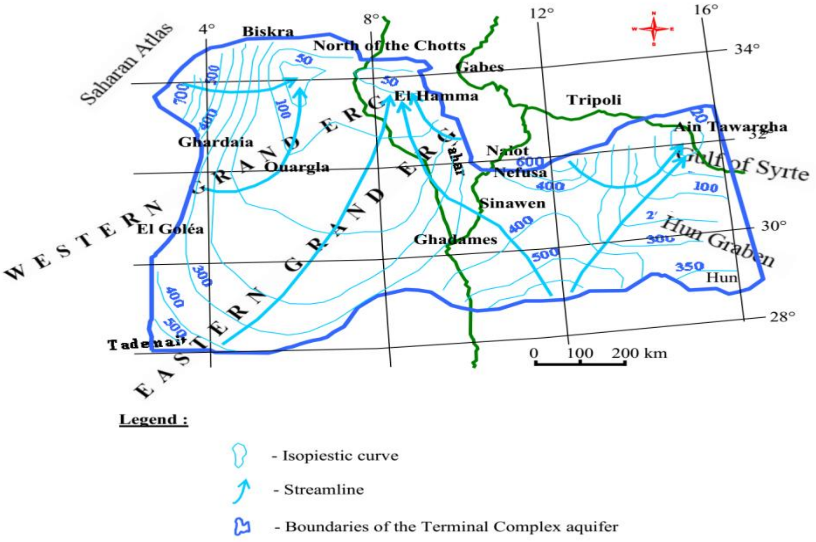


Fig. 2. Limits of the aquifer of the Complex Terminal with the piezometric levels and the flow directions

(Baba SY et al., 2006) (Repainted by Z. CHINI 2012).

According to the studies conducted on the hydraulic operation of the Complex Terminal shown in Figure 2, this water table covers an area of 350,000 km² (Slimani et al., 2017). Moreover, this complex is characterized by three more or less independent artesian aquifers, which have the following denominations: The first water table is about twenty meters thick, with a depth of 40 to 100 m depending on the region. The second water circulates about thirty meters thick. It reaches a depth of 100 m or more. The limestone water table, which is not yet exploited in all the study zones, is accessible to a reasonable depth, generally between 150 and 200 meters (Habes et al., 2016).

3. Analytical methods

Groundwater samples were collected. After sampling, electrical conductivity (EC) and pH were measured directly using digital devices. The chemical constituents of the water samples taken in the field were analyzed in the laboratory using standard methods suggested by the American Public Health Association. Ca^{2+}, Mg^{2+}, HCO_3^-, CO_3^{2-}, Cl^-, and TDS were analyzed by volumetric titration. EDTA at 0.05 N was used for the determination of Ca^{2+} and Mg^{2+} concentrations. 98% sulfuric acid was used to determine the concentrations of HCO_3^- and CO_3^{2-}. $AgNO_3$ 1 N was used to estimate the Cl^- (Seo et al., 2015). The measurement of Na^+, K^+, $SO4^{2-}$ ions was performed by flame photometry. NO_3^-, F, and SiO_2 were determined by UV-Vis spectrophotometric techniques.

4. Results and interpretations

The tested parameters are illustrated in Table 1, which combines the univariate statistical values for the chemical analyses of the Complex Terminal water along the Oued Righ region.

4.1 Hydrochemistry

4.1. 1. The Physico-chemical parameters

The pH of the Complex Terminal waters of the Oued Righ zone varied between 7.1 and 7.53, and it is characterized by an average value of 7.33 ± 0.14, i.e., pH values ranging from 5.5 to 8, which specify the majority of groundwater, et also fall within the standards set by the WHO (6.5-8.5). The concentration of carbon dioxide (CO_2) analyzed in water samples varied between 13.89 and 101.89 mg/l, with an average value of 32.42 ± 28.58 mg/l. The WHO has set the amount of CO_2 to be below 10 mg/l for good water quality (Zaiz et al., 2017). The temperature of the water table showed three aspects: excellent, average, and poor along the region. When it ranges between 18.9 and 30.1 with an average of 23.38 ± 5.25, this means that it respected the standard set by the WHO of 12 to 30 °C. The oxidation-reduction potential (Red/Ox) changes from one point to another from -20.9 to 1.5 mV, with an average of -7.93 ± 8.47 mV. Conductivity allows us to estimate the mineralization degree of water, as most of the dissolved matter in the water is in the form of electrically charged ions (Webster and Oliver, 2017). The analyzed waters had strong conductivity, varying from 2210.00 to 5830 µS/cm, with a mean value of 4796.25 ± 4796.25 µS/cm. Compared to the value set by the WHO of 500 to 1500 µS/cm, the results could be due to the water being moderately mineralized and saline. The salinity of the waters of the studied confined aquifer ranges from 1.1 to 3.2 mg/l, with an average of 2.6 ± 0.68 mg/l. TDS (Total Dissolved Solids) is the total concentration of dissolved substances in groundwater, ranging from 1112.00 to 3080.00, with an average value of 2395.25 ± 771.18 mg/l.

4.1. 2. Global mineralization

Water is said to be hard when the calcium ion is abundant. The dissolved content of calcium in the water table of the Complex Terminal ranged from 240.48 to 521.04 mg/l, with an average value of 422.84 ± 80.07 mg/l (Khebizi et al., 2020). The WHO sets a content of 100 mg/l of Ca^{2+} for good quality water (Saber, 2021). The average content of dissolved Mg^{2+} was 227.55 ± 55.95 mg/l, ranging from 109.37 to 281.94 mg/l. This range is significantly higher than the WHO standard (50 mg/l). Additionally, the waters from the Complex Terminal confined water table were less rich in magnesium than calcium, although both cations exceeded the standard of 50 mg/l.

The presence of carbonate in all the analyzed water samples was very homogeneous, represented by HCO_3^- concentrations ranging from 88.72 to 166.28 mg/l, with an average value of 123.37 ± 23.73 mg/l. These results comply with the WHO standard (250 mg/l). The average concentration of chloride ion (Cl^-) was 1008.38 ± 283.39 mg/l, ranging between 413.59 and 1372.57 mg/l. These levels significantly exceeded the WHO standard of 250 mg/l. The dissolved sulphates ranged from 700.00 to 1775.00 mg/l, with an average value of 1431.25 ± 354.5 mg/l. These results of SO_4^{2-} contents may locally exceed the permissible limit value of 250 mg/l.

4.1. 3. Pollution parameters

Pollution of the water table with pollutant substances can cause simple nuisance, making the water unsuitable for some human uses without posing a real danger to health (Tab. 1).

Table. 01 Mono-variable statistics for the chemical analysis of the Complex Terminal waters in Oued Righ region.

	WHO Standard	Mean	Standard Deviation	Minimum	Maximum	Variance
pH	6,5-8,5	7,33	0,14	7,10	7,53	0,02
Red/Ox (mv)	NA	-7,93	8,47	-20,90	1,50	71,75
Conductivity (µs/cm)	500-1500	4796,25	1175,39	2210,00	5830,00	1381541,07
Temperature (°C)	12-30	23,38	5,25	18,90	30,10	27,58
TDS (mg/l)	≤ 1000	2395,25	771,18	1112,00	3080,00	594723,36

Salinity (g/l)	NA	2,60	0,68	1,10	3,20	0,47
Free CO_2 (mg/l)	≤ 10	32,42	28,58	13,89	101,89	816,70
Ca^{+2} (mg/l)	≤ 100	422,84	80,07	240,48	521,04	6411,83
Mg^{+2} (mg/l)	≤ 50	227,55	55,95	109,37	281,94	3130,77
Cl^- (mg/l)	≤ 250	1008,38	283,39	413,99	1372,57	80307,25
SO_4^{-2} (mg/l)	≤ 250	1431,25	354,50	700,00	1775,00	125669,64
HCO_3^- (mg/l)	≤ 250	123,77	23,73	88,72	166,28	563,09
NO_2^- (mg/l)	≤ 0,5	1,88	3,44	0,00	10,00	11,84
NO_3^- (mg/l)	≤ 50	3,36	2,69	0,20	7,20	7,25
PO_4^{-3} (mg/l)	≤ 5	0,14	0,11	0,03	0,36	0,01
Total iron (mg/l)	≤ 0,3	0,20	0,16	0,07	0,51	0,02
Fluor (mg/l)	≤ 1,5	1,53	0,65	0,41	2,20	0,42

The waters of the Complex Terminal aquifer contain nitrogen compounds in two known forms: Nitrate and Nitrite. The NO_3^- ion ranged between 0.20 and 7.20 mg/l, with an average value of 3.36 ± 2.69 mg/l. These concentrations are well below the WHO standard of 50 mg/l. On the other hand, the NO_2^- ion content ranged between 0.00 and 10.00 mg/l, with an average value of 1.88 ± 3.44 mg/l. The NO_2^- ion content exceeds the WHO standard of 0.5 mg/l. The positive correlation between NO_3^- and Cl^- is less than 0.24, indicating the absence of pollution caused by mineral fertilizers. The concentration of phosphate ion (PO_4^{2-}) ranged between 0.03 and 0.36 mg/l, with a mean value of 0.14 ± 0.11 mg/l. The levels of PO_4^{2-} meet the WHO standard of 5 mg/l.

4.1. 4. Undesirable parameters

This part will focus on the study of undesirable parameters such as Iron and Fluorine in the waters of the Oued Righ Valley Complex Terminal. The iron content ranged from 0.07 to 0.51 mg/l, with an average value of 0.20 ± 0.16 mg/l. In some samples, the concentration of iron exceeds the WHO limit value of 0.30 mg/l. Fluorine, which has a WHO standard of 1.5 mg/l, has an average concentration in water samples of 1.53 ± 0.65 mg/l. The analyses applied to the water samples of the studied aquifer range from 0.41 to 2.20 (Qian et al., 2020).

4.2. Geochemical facies

4.2. 1. Physico-chemical parameters

The pH of the Complex Terminal waters in this region ranges between 6 and 8, which indicates a sedimentation medium that is generally close to neutrality, representing the intensity of acidity or alkalinity (Chebbah et allia, 2015). The pH and temperature of the Complex Terminal waters show positive correlations with the oxidation-reduction potential, with correlation coefficients of 0.53 and 0.54, respectively (Fig. 3).

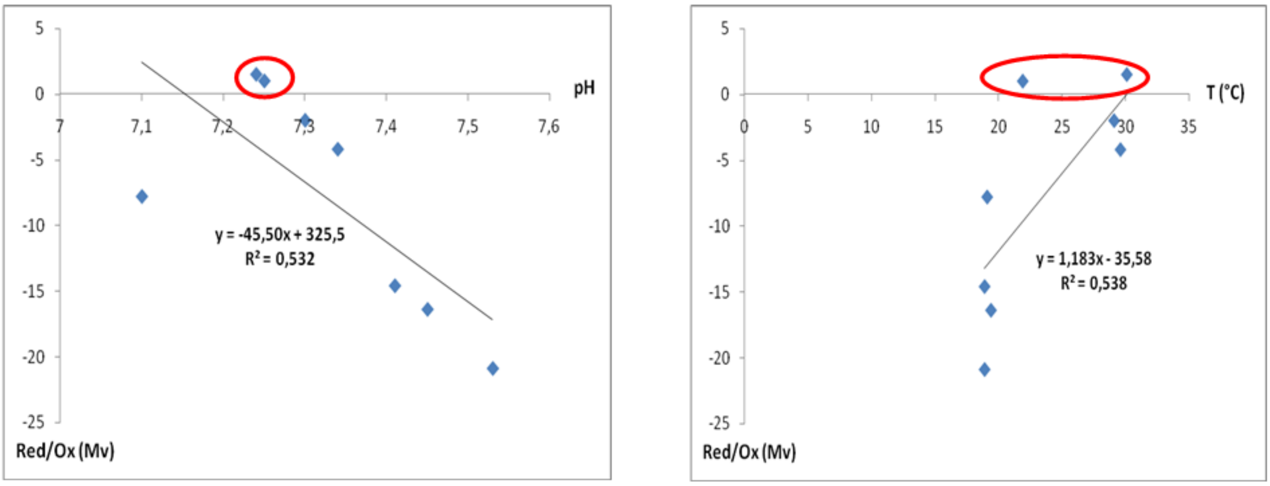


Fig. 3. The oxidation-reduction potential as a function of temperature and hydrogen potential

The oxidation-reduction potentials are mostly negative in all the samples, indicating that the medium becomes reduced in the absence of contact with air.

The oxidation-reduction potential based on pH is always negative (E = -0.03 pH), but in some cases, positive values are represented by circles. This phenomenon is due to various factors such as the intensity of biological activity, the oxidation state of certain elements (iron, manganese), the evolution of organic matter, and the abundance of individuals.

The high electrical conductivity (EC) values observed in the analysis results are due to the mineralization of groundwater, which can be explained by strong correlations between them. The origin of this mineralization is interpreted as the contact of Complex Terminal confined aquifer waters with certain geological formations (Fabre, 1976). Total dissolved solids (TDS) describe the inorganic salts dissolved in water and varied between 1112.00 and 3080.00 mg/l. TDS shows a strong correlation of 0.79 with electrical conductivity and salinity (Fig. 4).

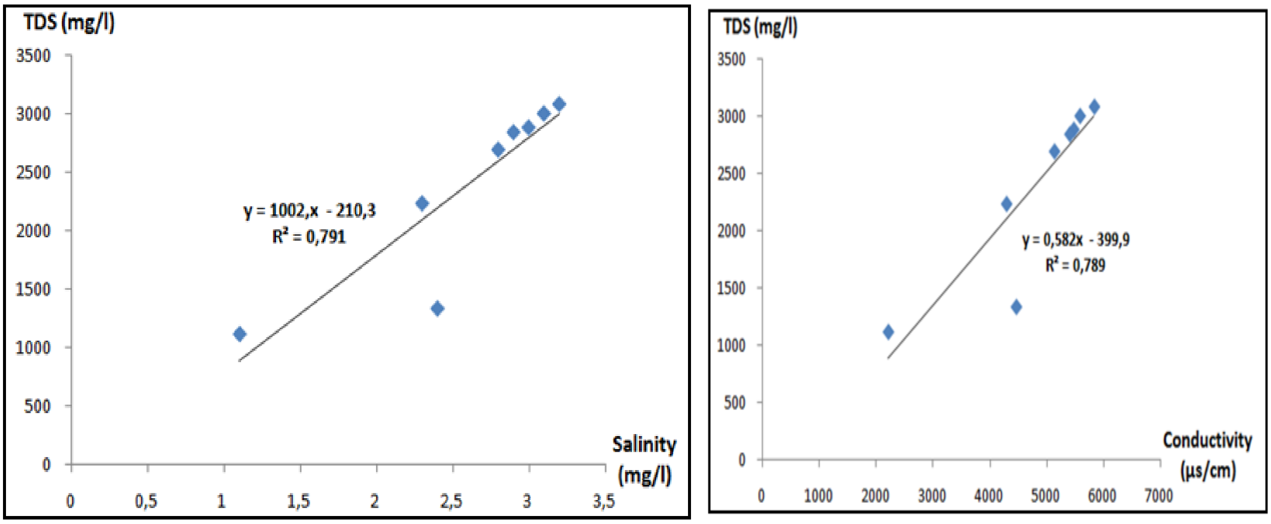


Fig. 4. TDS according to Salinity and Conductivity

4.2. 2. Global mineralization

The presence of calcium and magnesium ions can be attributed to the rock nature of the Complex Terminal aquifer, such as anhydrite gypsum. In some sampling points, appreciable quantities of alkaline earths (Ca^{2+} and Mg^{2+}) were observed, exceeding 500 mg/l and 250 mg/l, respectively. This can be explained by the contact with soils rich in calcium minerals. A positive correlation of 0.63 exists between calcium and magnesium ions (Fig. 5).

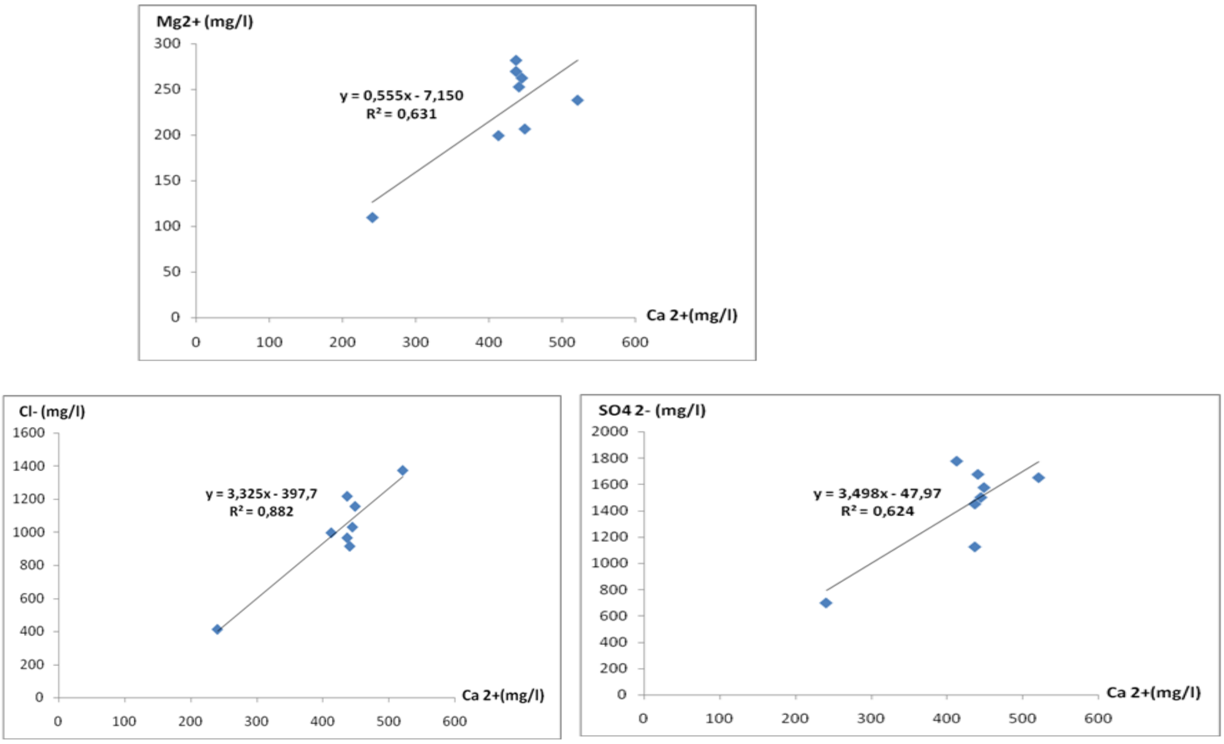


Fig. 5. Calcium with magnesium, chloride and sulphate

Calcium levels are relatively high in groundwater due to the geological characteristics of deep water tables. The presence of these ions in the Complex Terminal waters shows a positive correlation between calcium and other major elements (Mg^{2+}, Cl^{-}, and SO_4^{-2}), indicating their contribution to groundwater mineralization (Zaidi et al., 2021).

Sulphates in the groundwater primarily come from sources such as sulphide minerals, sulfur-containing organic products, and sulphated minerals. In the studied aquifer of the Oued Righ area, the sulphate content shows an average correlation of 0.56 with chloride ions and 0.62 with calcium ions. This relationship is mainly influenced by anhydrite, which is composed of calcium sulphate (Fig. 6). The presence of carbonates in the groundwater of the Complex Terminal aquifer can have several sources. It is explained by the presence of dolomite alteration, which consists primarily of calcium carbonate and magnesium ($CaMg(CO_3)_2$) with traces of Fe, Mn, Co, Pb, and Zn.

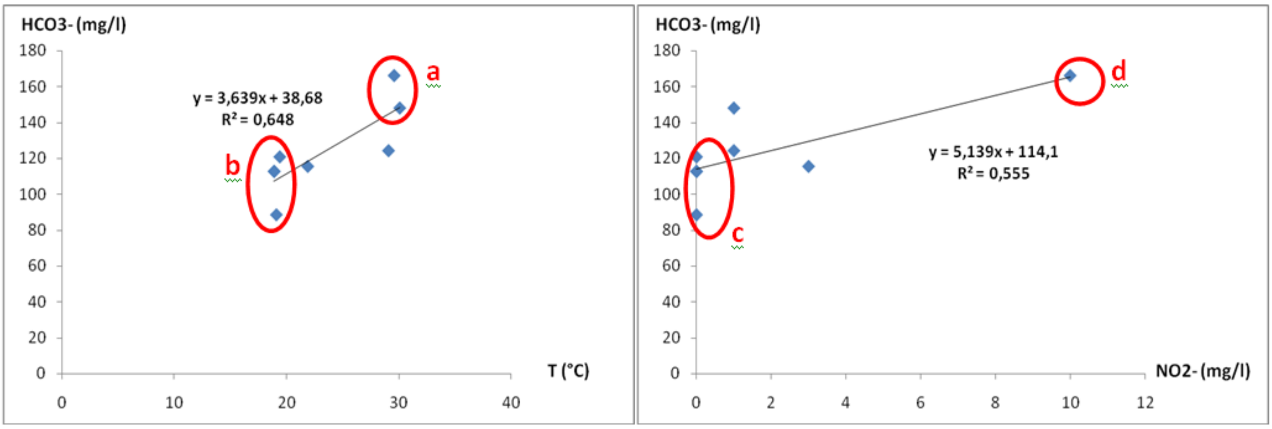


Fig. 6. Carbonate according to Temperature and Nitrite

Figure 6 shows a positive correlation of 0.65 between carbonate and temperature, indicating the influence of temperature on carbonate formation, which is more soluble at higher temperatures. Additionally, a positive association of 0.56 is observed between carbonates and nitrites. When nitrite concentrations are low (circle (c)), carbonate concentrations are also low, whereas high nitrite values (circle (d)) correspond to higher carbonate content.

4.2. 3. Pollution parameters

Nitrogenous compounds in water can serve as indicators of chemical pollution. In the Complex Terminal water, nitrate concentrations are very low, while nitrite concentrations exceed the WHO standard. Nitrite shows a positive correlation of 0.56 with carbonate. Normally, an impermeable layer that prevents the vertical penetration of surface pollutants (Wang et al, 2009) protects the Complex Terminal water. However, communication between the water table and the studied groundwater through cemented wells may be causing the presence of nitrite (Fig. 7). Orthophosphates (PO_4 ions) are the simplest and most common form of phosphates in water.

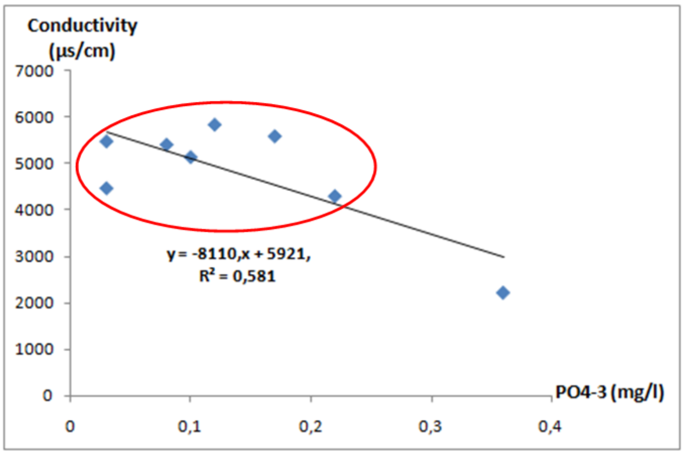


Fig. 7. **Conductivity depending on orthophosphate ion**

According to Figure 07, orthophosphate ions show an average positive correlation of 0.58 with electrical conductivity (EC), indicating that samples with low concentrations contribute to increased conductivity.

4.2. 4. Undesirable parameters

Iron is naturally present in rocks in various forms and can be found in groundwater. Human activities, such as drilling, can also contribute to increased iron concentrations in groundwater. Iron concentrations in the Complex Terminal confined aquifer range from 0 to 50 mg/l, while the WHO recommends iron levels below 0.3 mg/l. The presence of iron can promote bacterial growth and corrosion of pipes. Iron in the water shows multiple correlations, such as a strong positive correlation of 0.79 with orthophosphates, a correlation of 0.83 with sulfates, an average correlation of 0.5 with calcium, and strong positive correlations of 0.70 with both temperature and electrical conductivity (Fig. 8). These correlations are explained by the contribution of iron to mineralization and its association with various elements and physicochemical parameters (Gouaidia et al 2017).

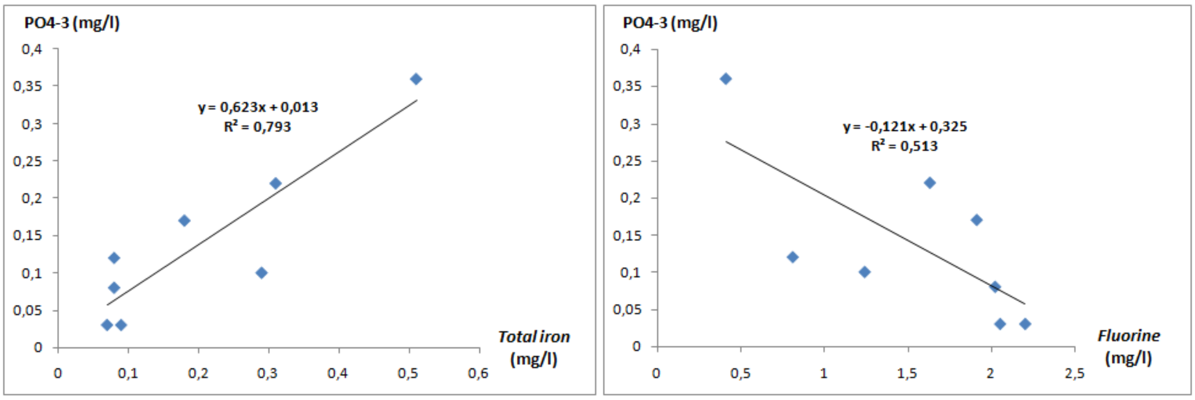


Fig. 8.Orthophosphate based on the total iron and fluorine

Fluorine concentrations were high in some sampling points in the groundwater of the studied confined aquifer (Kadri and Chaouche, 2018). The origin of fluorine is mainly dependent on the contact time of water with fluorinated minerals in the aquifer. In the Complex Terminal groundwater, fluorine concentrations ranged from 0.41 to 2.2 mg/l. Phosphate minerals primarily supply the fluoride ion in the aquifer, which explains the positive correlation of 0.51 with PO_4^{-2}. Fluorine also shows positive correlations with other parameters such as sulfates, total iron, calcium, temperature, and oxidation-reduction potential (Red/Ox), with correlation coefficients ranging from 0.41 to 0.59, indicating indirect relationships between these parameters.

4.2. 5. Origin of mineralization

The correlation is positive between Mg^{2+} and Ca^{2+} with a value of 0.63. This may be due to the fact that calcium solution is related to the presence of sulfate ions, which would essentially come from anhydrite composed of Calcium sulphate ($CaSO_4$), resulting in a positive correlation of 0.62 (Fig. 9).

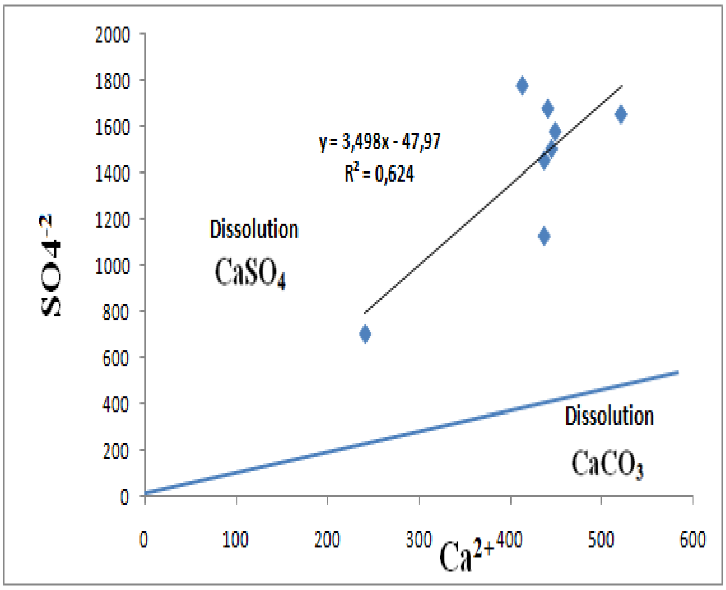


Fig. 9. Origin of excess calcium in the aquifer of the Complex

The analyzed water showed Ca^{2+} concentrations higher than those of Mg^{2+}. This could be explained by the contact of the water with the alteration of anhydrite gypsum, that is to say, the dissolution of calcium from the calcareous alteration is almost absent in the water of the studied confined aquifer. And the existence of excess calcium should be acquired by contact with gypsum formations (Fig. 10).

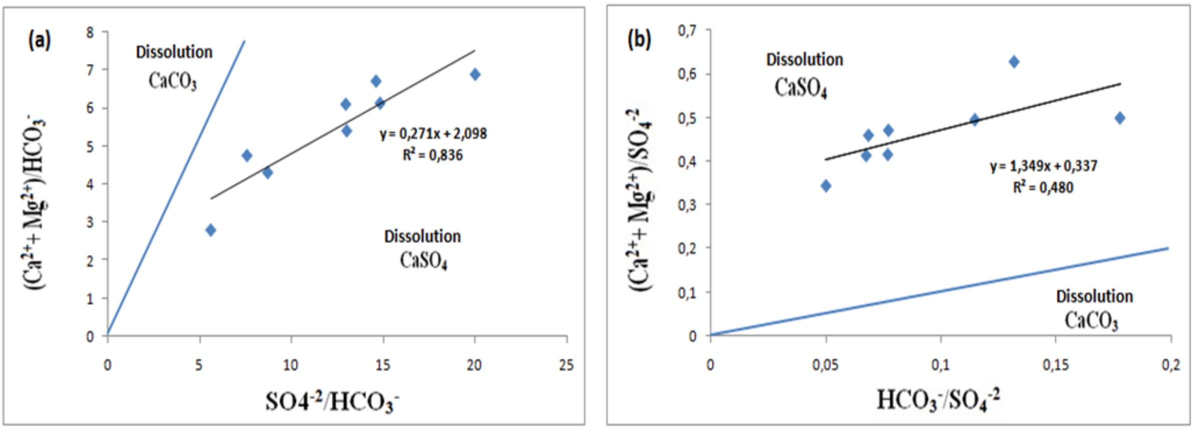


Fig. 10. Phenomena of water/rock interactions with gypses and carbonates in the Complex Terminal waters

The relationship between these various parameters (Figure 10) indicates the phenomena of interactions between the Complex Terminal water and the types of rock frequented. In this case, it may be said that during the discharge of groundwater gypsum type dissolution dominates to saturation before the carbonate. Due to impermeable facies formed essentially by clay, gypsum, and anhydrite, Ie the incoming waters are already saturated, which can be interpreted by the low positive correlations of the carbonate with the other parameters. Study of the soil solution : In the arid regions characterized by a dry season large enough that the wet season, irrigation by groundwater considered as a first source (Madhav et al., 2018), (Aravinthasamy et al., 2020). The statistical values monovariables for the data for the analyzes made on the soil solution, are illustrated in the following table (Tab. 2).

Tab. 02 The statistical values monovariables for the data for the analyzes made on the soil solution

	pH	**Conductivity (mmohos/cm)**	**HCO_3^{2-} (meq/l)**	**CO_3^{2-} (meq/l)**	**SO_4^{2-} (meq/l)**	**Cl^- (meq/l)**	**Ca^{2+} (meq/l)**	**Mg^{2+} (meq/l)**	**Na^+ (meq/l)**	**K^+ (meq/l)**
Average	7,68	16,84	3,47	1,26	84,10	254,76	43,38	70,18	190,48	5,36
Standard deviation	0,33	20,86	2,45	13,91	143,41	421,20	10,19	115,71	310,54	9,43
Minimum	6,00	3,01	0	0	4	11	6	3,50	1,80	0
Maximum	8,80	146	15	184	1776	3610	85	1050	2775	65

CV %	0,04	1,24	0,70	11,07	1,71	1,65	0,23	1,65	1,63	1,76

The study of the acidity of the soil (pH): Acidification is a decrease in the H^+ ions in the soil solution or the tendency of the complex clayey-humic to attach significant quantities of H^+ ions to the detriment of mineral cations. The effects of acidification are harmful both to the plants and the soil. We observe decreases in yields, variations in the chemical composition of plants, a slower breakdown of organic matter, a decrease in biological activity and enzymatic activity, a loss of effectiveness of some herbicides, and, in extreme cases, a collapse of the structure. The following mapping (Fig. 11) concerning the pH property is done using the method of kriging along the region of Oued Righ (Kumar et al., 2007), (Seyedmohammadi et al., 2016).

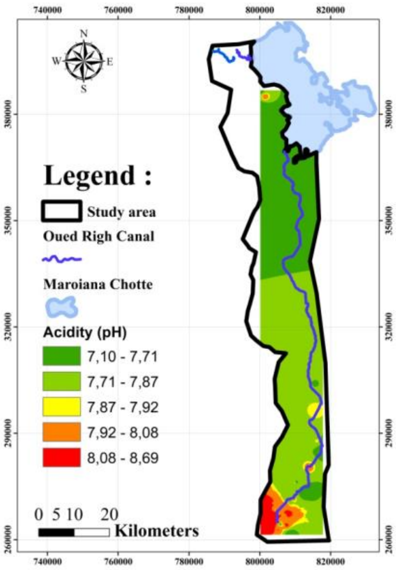


Fig. 11. Interpolation of the pH by the kriging method in Oued Righ region.

The levels of soil acidity are measured by the pH, which usually varies between 4.5 to 8.5 inversely proportional to the concentration of H^+ ions. It is expressed with reaction classes according to table 3

Table 3: Classes of reaction depending on the pH of the soil.

Classes of reaction	The pH values
Extremely acidic	≤ 4,5
Very Strongly acid	4,6 - 5,0
Strongly acid	5,1 - 5,5
Acid medium	5,6 - 6,0
Weak acid	6,1 - 6,5

Neutra	6,6 - 7,3
Weakly alkaline	7,4 - 7,8
Oderately	7,0 - 8,4
Strongly alkaline	≥ 8,5

According to the analysis of the soil pH presented in figure 11, the pH in the majority of the Oued Righ region is generally low alkaline, ranging between 7.4 to 7.8. There is a moderate alkalinity of 7 to 8.4 in the Sidi Slimane and Megarine areas, southwest of Blidet Amor, and north of the Valley of Righ (Chott Merouane). However, in the western part between Djamaa and M'ghier, the pH is characterized as neutral and weakly acidic. In the extreme southwest of Blidet Amor, the pH is strongly alkaline (≥ 8.5). According to the soil pH results for the Valley of Righ, they are acceptable for agricultural exploitation since no plant tolerates a pH less than 3 or greater than 9, and the majority of cultivated plants require a pH between 5.5 and 6.5 depending on the species.

Study of Salinity

The determination of soil salinity is based on the principle of extracting an electrolyte, which measures the concentration of dissolved elements using various methods. It is often useful to know the salt quantity present in irrigation water, water absorbed by the soil, or water from wells when considering a soil sample overall (AL-Musawi, 2014), (Azlaoui et al., 2021). This can be done by directly measuring the electrical conductivity, which is a fast and reliable method for estimating the overall salt content in the solution, also known as the degree of mineralization (Venkatramanan et al., 2016). The physico-chemistry of electrolyte solutions provides the necessary information for calculating the electrical conductivity of a solution based on its chemical composition, specifically considering the molar conductivity equivalent of ions (Adhikary et al., 2009), (Geilfus, 2018). The following mapping (Fig. 12) concerning the property of electrical conductivity is made using the kriging method along the Oued Righ region.

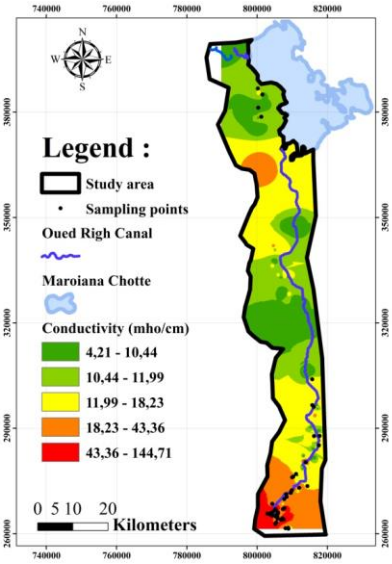


Fig. 12. Interpolation of electrical conductivity using the kriging method in the Oued Righ region.

Salinization refers to the accumulation of salts in the soil (Mathieu and Pieltain 2003) have established a scale of soil salinity with four classes based on the aqueous extract (1/5) (Tab. 4):

Table 4 : Classes of soil salinity based on the aqueous extract.

Classes of Soil Salinity	Values of conductivity in (dS/m or mmho/cm)
Soils not salted	0.17 - 0.35
Salty soils	1.5
Soils are very salted	2.23-3.17
Soils extremely salted	4.23 -12.52

Ion balance of the soil solution: Salts: Neutral salts (Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, CO_3^{2-}, HCO_3^-, Cl^-) can accumulate in soils depending on the intensity of irrigation, and their toxicity can damage plants and reduce water availability (Ghazaryan and Chen, 2016). To understand the types of harmful salts present in the soils of the Oued Righ region, we conducted simple correlations between the cations and anions in different soil samples (Tab. 5). The correlation coefficients are summarized in the following table.

Table 5: Correlation coefficients for cations and anions in the soil solution of Oued Righ region.

R^2	CO_3H^-	CO_3^{-2}	SO_4^{-2}	Cl^-

Ca^{+2}	0,067	0,004	0,025	0,065
Mg^{+2}	0,405	0,000	0,546	0,900
Na^{+}	0,321	0,000	0,522	0,985
K^{+}	0,067	0,067	0,566	0,869

According to the results shown in table 5, we observe that the Oued Righ region is characterized by the accumulation of NaCl as the dominant salt in the soil, with a correlation coefficient of 0.985 between chloride ions and sodium cations. This is followed by semi-dominant salts such as $MgCl_2$ and KCl, with correlation coefficients of 0.90 and 0.87, respectively. Salts present in moderate quantities, such as K_2SO_4, $MgSO_4$, and Na_2SO_4, exhibit correlation coefficients around 0.54. $Mg(HCO_3)_2$ and $NaHCO_3$ show moderate affinity, while other potential salts display weaker correlations. The values of correlation coefficients indicate limited relationships between them.

Conductivity (mmhos/cm): Salty soils are widespread across continents and climates. The global expansion of irrigated agriculture often leads to secondary land salinization due to chemical degradation, physical soil properties, and improper irrigation practices (Al-Hadithi et al., 2019).

To determine soil salinity and understand the interactions between cations and anions affecting variations in electrical conductivity, we directly measured the water extracted from the soil (Jena et al., 2013). Based on the experimental results, we calculated simple correlations between electrical conductivity and cations/anions, as summarized in the following table 6

Table 6: Correlation coefficients between electrical conductivity and cations/anions in the soil solution of the Oued Righ region.

R^2	Cl^-	SO_4^{-2}	Mg^{+2}	Na^+	K^+
Conductivité électrique	0,95	0,76	0,74	0,94	0,88

The interpolation of our data using the Kriging method (a geostatistical method) allows us to generate maps of electrical conductivity, cations, and anions in the soil solution (Montero et al., 2015), Figure 13 shows the interpolation of electrical conductivity, cations, and anions in the Oued Righ region.

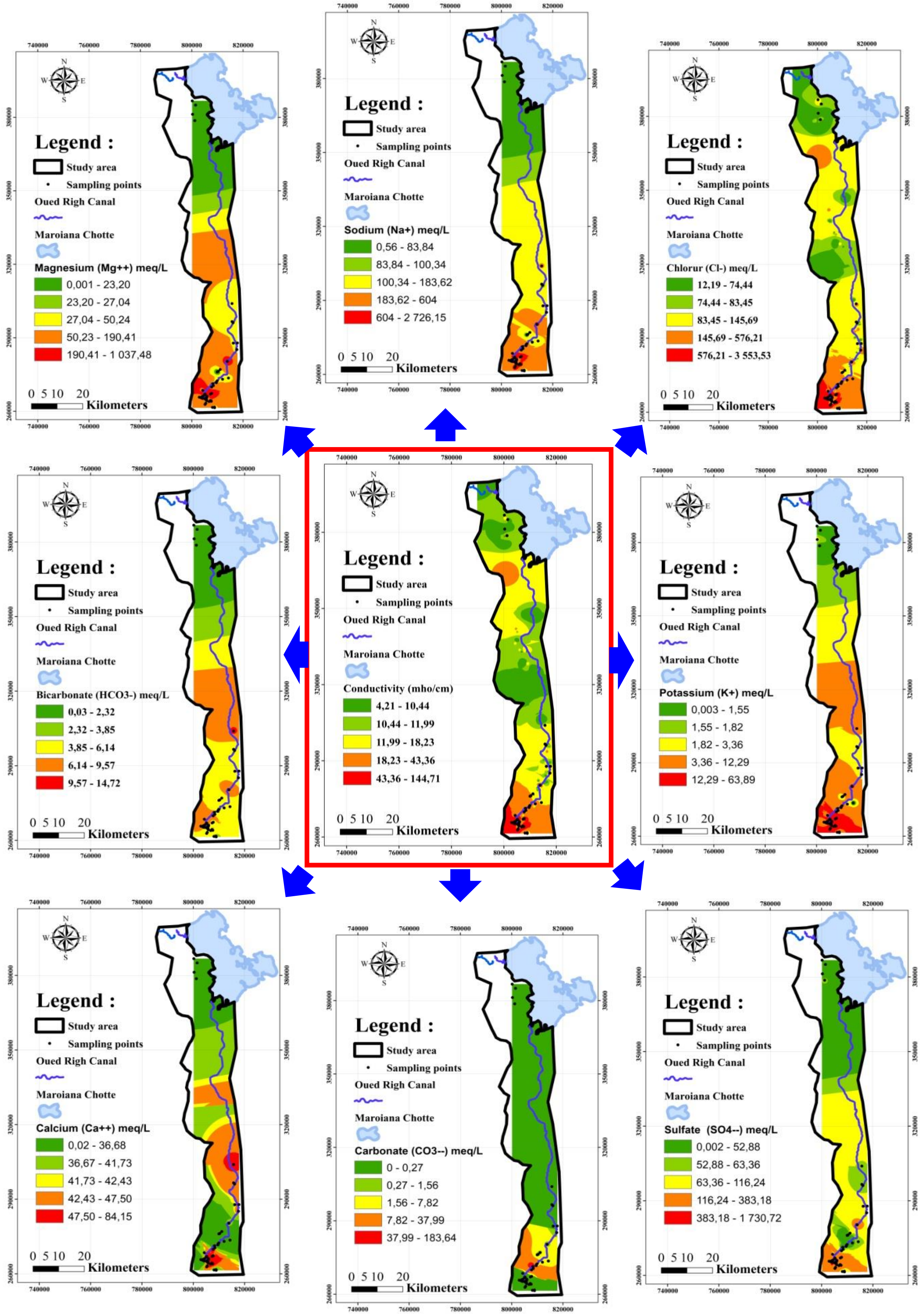


Fig. 13. Interpolation by the method of kriging of the electrical conductivity and the cations and anions for the solution of the soil in the region of Oued Righ.

We observe that electrical conductivity is primarily linked to the presence of chloride ions and sodium cations, with correlation coefficients of 0.95 and 0.94, respectively. The maps also exhibit similar patterns, indicating the prevalence of NaCl in the soil. There is also a significant affinity between electrical conductivity and potassium cations, with a correlation coefficient of 0.88, suggesting the possible presence of salts such as KCl and K_2SO_4 in the Oued Righ region. Additionally, manganese cations and sulfate anions show correlations of 0.74 and 0.76, respectively, with electrical conductivity (Gharbi et al., 2019). These results provide insights into the presence of different salts, such as $MgCl_2$, K_2SO_4, $MgSO_4$, and Na_2SO_4, in the soil, and their influence on electrical conductivity varies based on the calculated correlation coefficients. Figure 14 below illustrates the variation of electrical conductivity as a function of chloride ions in the water extracted from the soil across the Oued Righ region.

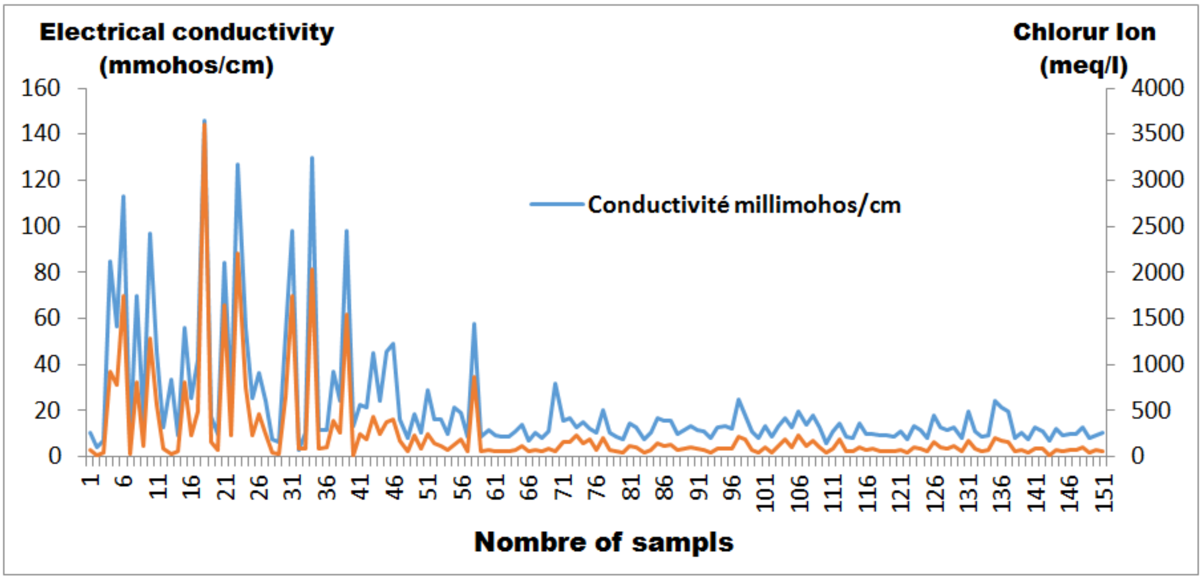


Fig. 14. Variations of the electrical conductivity as a function of Cl^- ions in the soil solution of the region of Oued Righ.

The pace of this curve confirms the overlay for each sample between the electrical conductivity and the ions of Cl^-, what we confirms the presence of NaCl salt with a percentage majority.

Origin of Salinity

Operating Procedure

Start by placing a quantity of 100 g of salted soil into a beaker. Add distilled water to the beaker until the water level is sufficient to cover the salted soil (Fig. 15). Use a magnetic stirrer for gentle agitation to mix the water and salted soil, allowing the salts to dissolve into the water. After thoroughly stirring the mixture, pour it into a filter to separate the sand. The sand will remain in the upper part of the filter, while the salt solution (saltwater) will pass through the filter and be collected in a clean container.

Next, place the container in an oven or an incubator at a temperature of 105°C. Once all the water has evaporated, crystals of salt will be obtained in the container. As the salt is now in crystal form, it needs to be dried to eliminate any remaining moisture and reduce the risk of contamination.

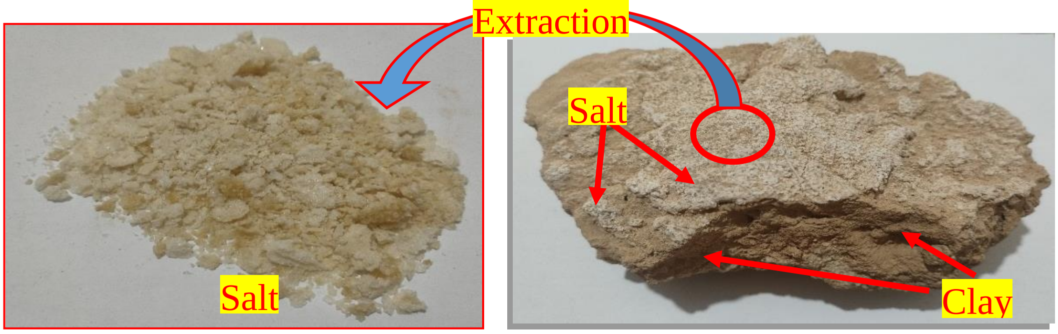
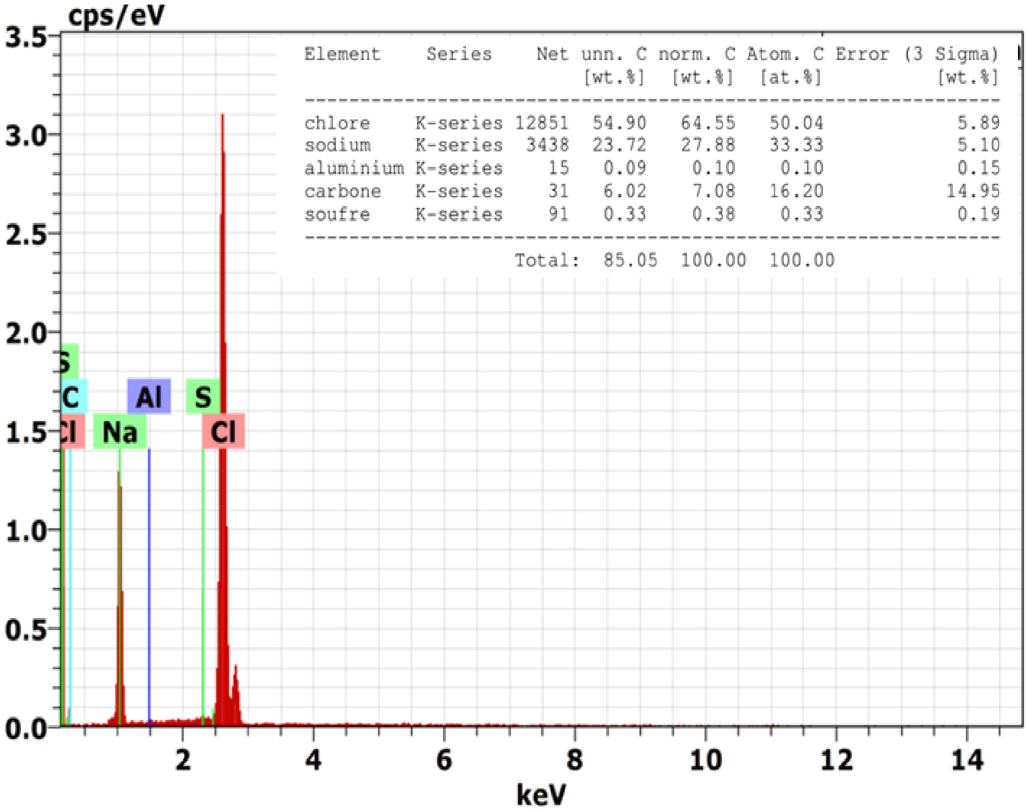


Fig. 15 Analysis of the elemental composition of the salt sample by EDX.

The obtained salts are ready for analysis using Energy Dispersive X-ray Spectroscopy (EDX), a commonly used technique for determining the elemental composition of solid samples, including salts. The figure 16 represents the EDX spectrum obtained during this analysis:



```
Element     Series    Net unn. C norm. C Atom. C Error (3 Sigma)
                          [wt.%]  [wt.%]  [at.%]          [wt.%]
-----------------------------------------------------------------
chlore     K-series 12851  54.90   64.55   50.04            5.89
sodium     K-series  3438  23.72   27.88   33.33            5.10
aluminium  K-series    15   0.09    0.10    0.10            0.15
carbone    K-series    31   6.02    7.08   16.20           14.95
soufre     K-series    91   0.33    0.38    0.33            0.19
-----------------------------------------------------------------
                   Total:  85.05  100.00  100.00
```

Fig. 16 Analysis of the elemental composition of the salt sample by EDX.

The peaks in the EDX analysis of the sample will help identify the constituent elements of the salt, providing information about their elemental composition. The EDX analysis results show that the characteristic chloride peak present in the salt sample constitutes a significant percentage, with a concentration of 64.55%. On the other hand, sodium ions (Na^+) make up almost half of the Cl^- percentage, with a value of 27.88%. This explains that the main nature of the salts is NaCl (sodium chloride), while the remaining chloride ions are combined with cations to form salts of other types.

Conclusion

The hydrochemical study of the Complex Terminal aquifer reveals that the water is moderately mineralized, with a conductivity higher than 4796.25 µS/cm² on average. The salinity is primarily influenced by chloride ions, indicating a process of water mineralization resulting from the interaction between water and aquifer rock.

The pH of the water is generally neutral, ranging between 7.1 and 7.53, which falls within the recommended standard of 6.5-8.5 by the World Health Organization (WHO). However, the analysis shows a carbon dioxide concentration ranging from 13.89 to 101.89 mg/l, exceeding the WHO's guideline of less than 10 mg/l for good quality water (Tabouche and Achour, 2010).

The concentration of calcium in the water ranges from 240.48 to 521.04 mg/l, exceeding the WHO's limit of 100 mg/l. The dissolved magnesium (Mg^{2+}) content varies between 109.37 and 281.94 mg/l, indicating that it does not meet the recommended standard of 50 mg/l. The water is found to be richer in calcium ions compared to magnesium ions.

The chloride and sulfate ions in the confined aquifer of the Complex Terminal show concentrations higher than the WHO's recommended value of 250 mg/l. Chloride concentrations range from 413.59 to 1372.57 mg/l, while sulfate ion concentrations range from 700.00 to 1775.00 mg/l. Carbonate concentrations range from 88.72 to 166.28 mg/l, meeting the WHO's standard of 250 mg/l.

Nitrate and orthophosphate concentrations in the water range from 0.20 to 7.20 mg/l and 0.03 to 0.36 mg/l, respectively. These values are lower than the WHO's limit values of 50 mg/l for nitrate and 0.5 mg/l for orthophosphate, indicating that they are permissible for consumption. However, nitrite exceeds the acceptable standard of 0.5 mg/l, with a value of 10 mg/l. The statistical analyses suggest a low correlation between nitrate and chloride ions, indicating a lack of pollution from mineral fertilizers.

The mineralization is attributed to the correlation between calcium and sulfate ions, which originate from the alteration of anhydrite composed of natural calcium sulfate. The higher concentration of calcium compared to magnesium suggests minimal contact of water with gypsum anhydrite alteration and the absence of significant dissolution of calcium from limestone alteration.

In conclusion, the water from the Complex Terminal aquifer in the Oued Righ area is suitable for agricultural and domestic use for daily activities. However, for human consumption, it is only permitted for external use.

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