ESTIMATION OF GROUNDWATER RECHARGE IN ARID REGION THROUGH HYDROCHEMISTRY AND ISOTOPE A CASE STUDY KOURIMAT BASIN MOROCCO

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ABSTRACT

Morocco is classified as an arid to semi-arid country with a population according to 2013 estimates of 35 million inhabitants and a growth rate of 1,4 %. Efficient use of Morocco's scarce water is becoming increasingly important as the urban population grows. This study concerns the groundwater recharge in the Kourimat basin and describes a combined methodology for groundwater recharge estimation in Morocco, through the isotopic and hydrochemical approaches.

Groundwater samples from Essaouira basin, east Morocco, falls along the Global Meteoric Water Line (GMWL), and below the Local Meteoric Water Line (LMWL), suggesting that the waters have been recharged under a different climatic regime, different from today.

Water isotopic composition shows low evaporation of precipitations during infiltration. Depletion in heavy isotopes is the characteristic of mountain rainfalls or of a climate colder and wetter than present at the research area. Carbon-14 activities (30 – 60 pMC) indicate a long residence time.

Tritium levels in the groundwater of the Kourimat Basin are below the detection limit (<1.5 TU). Five groundwater samples in South-West of Essaouira city, presents tritium content between 1 and 3 TU.

Keywords: Kourimat Basin, Arid climate, groundwater resources, stable and radioactive isotopes, Morocco.

INTRODUCTION

The countries of North Africa have long had the challenge of providing sustainable liveihoods for their populations in the fragile ecosystems of semi-arid and arid areas, facing the challenging issues of water scarcity, drought, land degradation and desertification. Climate change is a reality in North Africa and it places additional constraints on its fragile ecosystems and limited natural resources. The most common and high-impact manifestations of local climate variability in the North Africa involve temperature and precipitation, which have marked effects on local and regional economies and livelihoods. 2010 was the warmest year on record in North Africa.

The Kourimat basin is situated between Ait Daoud in the south and Jbel Hadid in the north. The basin is installed in a syncline structure open to the Atlantic Ocean. The region has a population of around 400 000 inhabitants and is predominantly rural. The basin area is about 6000 Km^2 and is characterized by limited and discontinuous water resources. Considering the water demand of the region is crucial, therefore, identify and characterize potential new areas for groundwater supply in order to build an integrated water management projects.

The objective of this study was the application of chemical and isotopic methodologies in the identification and characterization of possible interconnections between aquifer in the Meskala region (Turonian aquifer and Plioquaternary; quantify if possible the percentage of mixing between the different systems; and groundwater dating through radiocarbon content in the coastal zone and Meskala region aquifers (Figure 1).
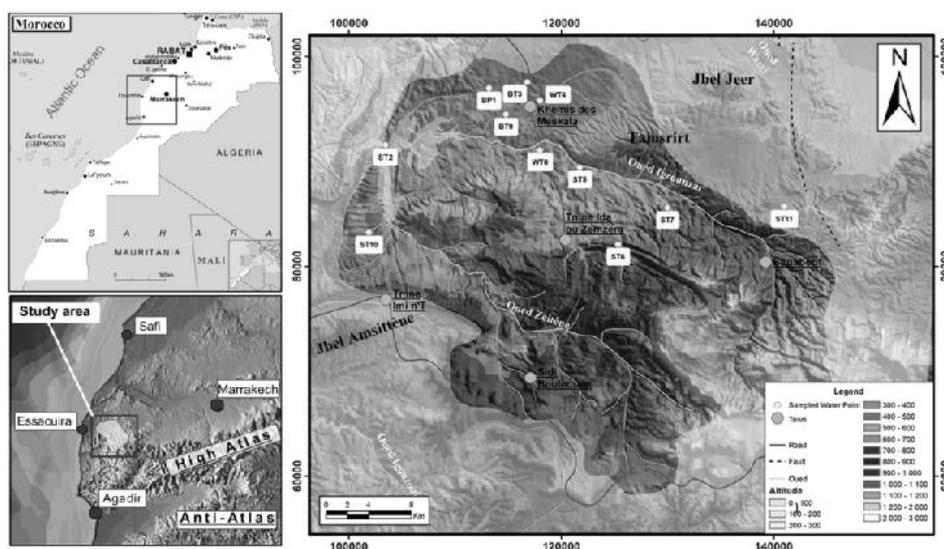
Figure 1: Localization of study area (El Moukhayar et al., 2014).

CLIMATIC AND HYDROGEOLOGICAL SETTING

The climate of the coastal region of Essaouira is a highly original and particular due to the action of cold Canary Current which moderates temperature amplitudes type and gives the Essaouira region a climate of insular and semi-arid, exceptional in Morocco.

In the study area most of the rain falls between October and early spring. The climate is typically semi-arid with an annual average rainfall about 300 mm/year (Figure 2), which is some 30% less than half a century ago, a trend that is common to the whole of Morocco.
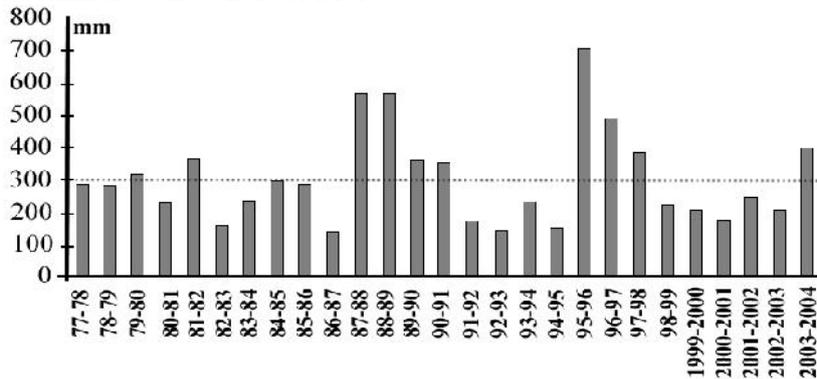
Figure 2: Precipitation in Igrounzar station (mm/year)

The research region is characterized by a "cool" dry season, followed by a "hot" dry season, and ultimately by a "moderate" rainy season. In general, there are significant diurnal temperature fluctuations within these seasons. Quite often, during the "cool" dry season, these diurnal temperature fluctuations (Figure 3) restrict the growth of plant species, with 2390, 6 mm / year evaporation measured by COLORADO pan in Igrounzar station.
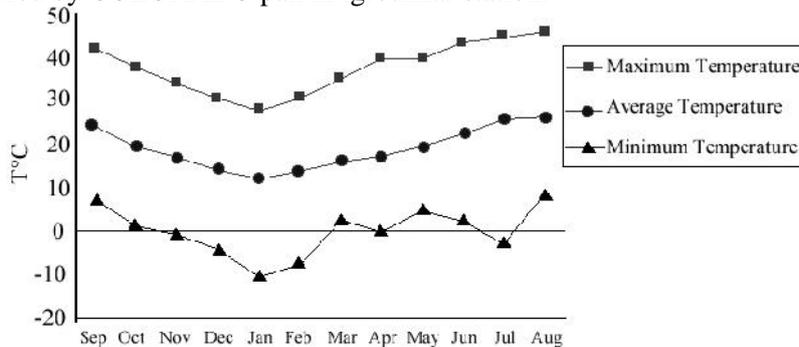
Figure 3: Average temperature per month in Igrounzar station**.**

The Meskala region of the Essaouira Basin is primarily characterized by sedimentary formations of late Palaeozoic to early Cenezoic age with the greatest thickness being of Mesozoic age. The Ceno-Turonian aquifer is mainly composed by calco-dolomitic layers. The Ceno-Turonian formations constitute a highly permeable dolomite and limestone aquifer in the study area, which explains its use recently drilled for supply for the city of Essaouira.
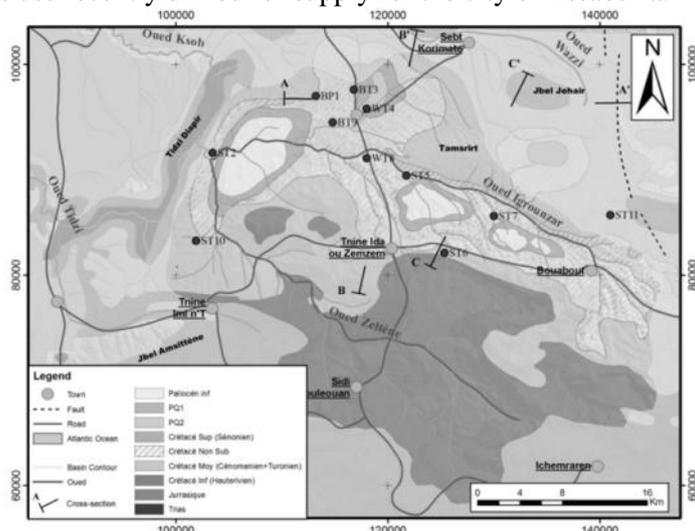
Figure 4: Geological map of study area (Geological background revised from Geological map of Morocco)

The main source of water in the Ceno-Turonian aquifer is believed to be the rain that falls on the foothills Kourimat area The westward movement of ground water from the mountainous outcrop areas appears to be impeded by a zone of low permeability related to structural and stratigraphic features of this region along the western side (Figures 4, 5 and 6).
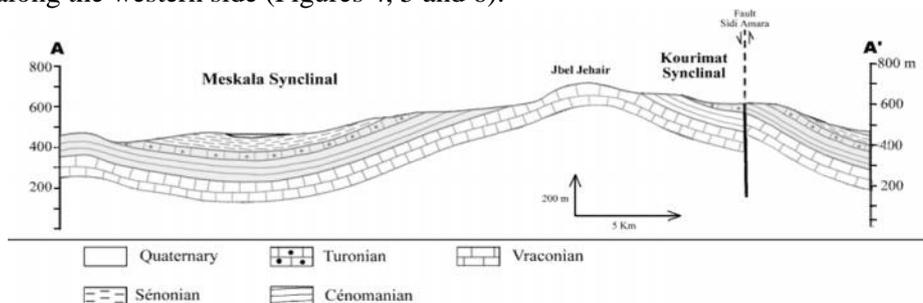
Figure 5: Schematic section showing the geological limits of aquifers in Meskala and Kourimat (Jalal, 2001)
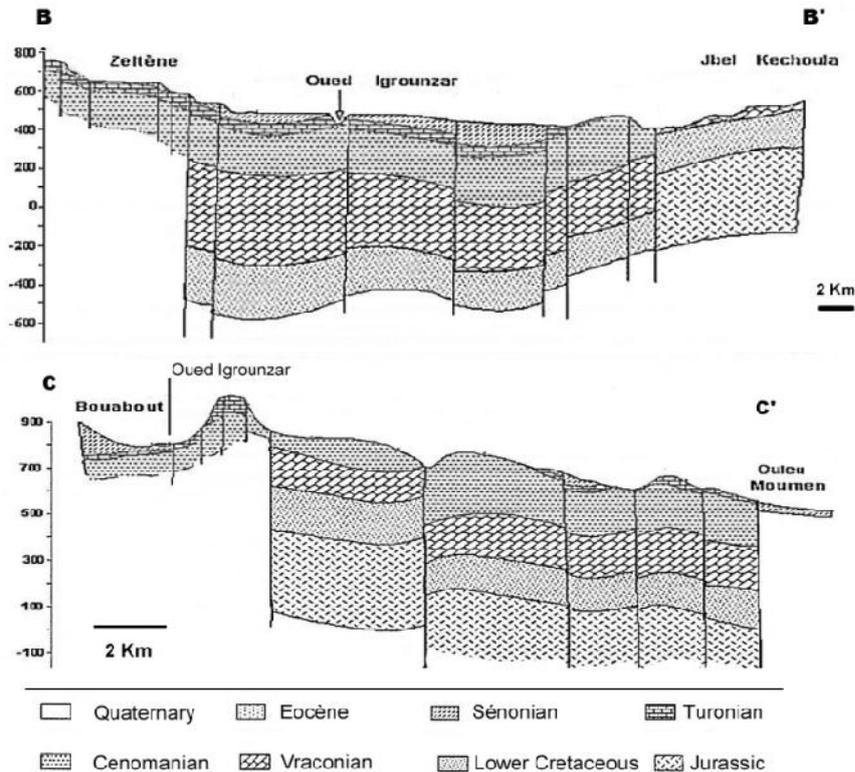
Figure 6: Schematic section showing the geological limits of aquifers Oued Igrounzar (Jalal, 2001)

SAMPLING AND METHODS

To determine the possible existence of an interconnections between aquifers in the Meskala region and to quantify the percentage of this mixing in the Kourimat Basin10 groundwater samples have been collected, in springs and in water points spreading out to the Upstream (wells and boreholes)to perform chemical and isotopic analyses. The samplingpoints are shown in (Fig. 1).All samples have been subjected to physical and chemical analyses. Physico-chemical parameters (temperature, pH, electrical conductivity (E.C)) were measured in the field, alkalinity in the laboratory shortly after sampling, othermajor ions (Ca^{2+}, Mg^{2+},Na^{+}, K^{+}, Cl^{-}, SO_4^{2-},NO_3^{-}) were determined in the laboratory at the University of Marrakech, Morocco (Table 1).

The stable isotope analyses, ^2H (‰), ^{18}O (‰ VSMOW) and ^{13}C (‰ VPDB), were performed by mass spectrometry, and the radiocarbon (^{14}C) analyses by liquid scintillation counter, reported as percentage modern carbon (pMC). These

determinations were performed in the International Atomic Energy Agency – Isotope Hydrology Laboratory in Vienna (AIEA–IHLS)(Table 2).

Stable isotope composition of water samples (^{18}O, ^{2}H) was determined at the Laboratory by Laser spectrometry measurement. The results are expressed as relative deviations (in per mil (‰)) from the Vienna Standard Mean Ocean Water (VSMOW). The analytical precision (1) was in the order of 0.1‰ for ^{18}O and 1‰ for ^{2}H. The carbon-14 determinations were made on the TDIC (Total Dissolved Inorganic Carbon) of groundwater, precipitated in the field as $BaCO_3$ at a pH higher than 9.0. The counting rates of the ^{14}C (benzene) were measured using a liquid scintillation counter. ^{14}C content is expressed in pMC (percentage of modern carbon). The errors associated with this method vary with the amount of carbon available in each sample, and increase where ^{14}C content is low. The ^{13}C values are reported in ‰ to V-PDB (Vienna–Peedee Belemnite) standard, with an accuracy of ±0.1‰.

Evaluation of the groundwater data was carried out by statistical methods, and afterwards, geochemical and isotopic methods were used to establish / identify the processes controlling the groundwater chemistry, i.e. in the identification and characterization of water-rock interaction mechanisms present within the aquifer system. The concentrations of major ions in groundwater may be correlated based on underlying physical and chemical processes. Hierarchical Cluster analysis (HCA) was used to identify natural groupings in a dataset according to chemical dissimilarity of the samples (Farnham et al., 2000; Kuells et al., 2000; Alberto et al., 2001; Güler and Thyne, 2004; Thyne et al., 2004).

The hierarchical clustering approach was developed through a combination of the Ward's linkage method (Ward, 1963) and squared euclidean distances as a measure of dissimilarity between the water samples. This statistical analysis will produce a graphical representation or dendrogram of individual groups, containing samples with close values of parameters. The HCA was completed by a PCA. This technique is used to distinguish different groups of geochemical variables according to their degree of co-variation. In our case the aim of PCA was to associate a large number of observed variables into a smaller number of factors (components) that can be more readily interpreted as these underlying processes (Mathes and Rasmussen, 2006; Lorite-Herrera et al., 2009). Both HCA and PCA were performed using XLSTAT statistical software.

The evolution of geochemical processes in groundwater depends on the equilibrium between mineral phases and water and is commonly discussed by saturation indices. A positive value of saturation indices computed with respect to solid phase, following Garrels and Christ (1965), indicates an oversaturated state. In our case, saturation indices have been calculated from most common minerals encountered in the aquifer formation meant calcite, dolomite, halite and gypsum using DIAGRAM software (Appelo and Postma, 1996).

RESULTS AND DISCUSSION

Chemical results

The hydrodynamic study allowed us to characterize the flow and get a first grasp of the aquifers. This relationship has been further clarified in the hydrochemical study. The piezometric study is in large part based on piezometric data collected during the 2006 and 2007 companion and D.R.H data. From Figure 7 it is possible to identify a main direction of the groundwater towards Atlantic Ocean, from SE-NW (Figure 7)
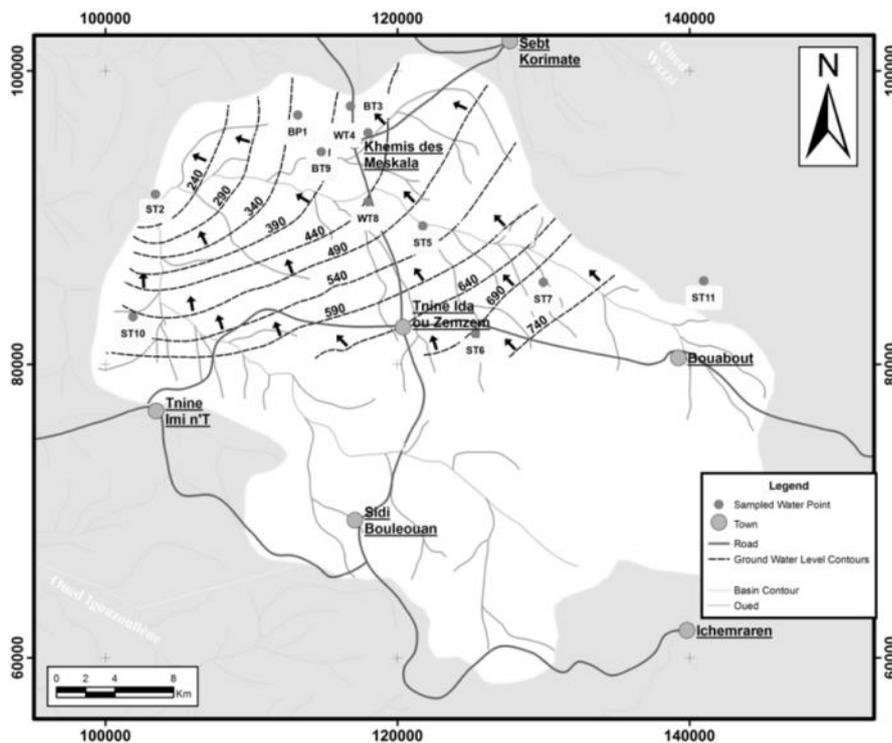
Figure 7: Location of sampled points and piezometric contour map
(Piezometric background -D.R.H- Revised)

The study of the hydrogeochemical evolution of the groundwater along its flow path is important not only to to identify the chemical facies of the waters and try to insert them within a water-rock interaction processes but, also from the practical point of view, i.e. into the quality of potability and their suitability for irrigation. It this studymonitors also the spatial evolution of physicochemical

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parameters within the aquifer and estimates their origin correlating with the geology and piezometric, allowing this to obtain information regarding the possible mixing mechanism between aquifer systems.Water aquifer points are intended for drinking water and for irrigation of agricultural land. Water to be used must meet certain standards that vary by type of use.

Table 1 shows the variability and magnitude of various physicochemical parameters of groundwater across the study area. The groundwater samples do not present a very high electrical conductivity, the values found in the groundwater samples from Turonian aquifer, varies from 1000 µS/cm to the 2500 µS/cm (Figure 8), with an average of 1500 µS/cm.The most interesting is that the higher mineralization are not found near the coastline but near the inland limit of the Kourimat Basin, point to an addition source of salt to the system.
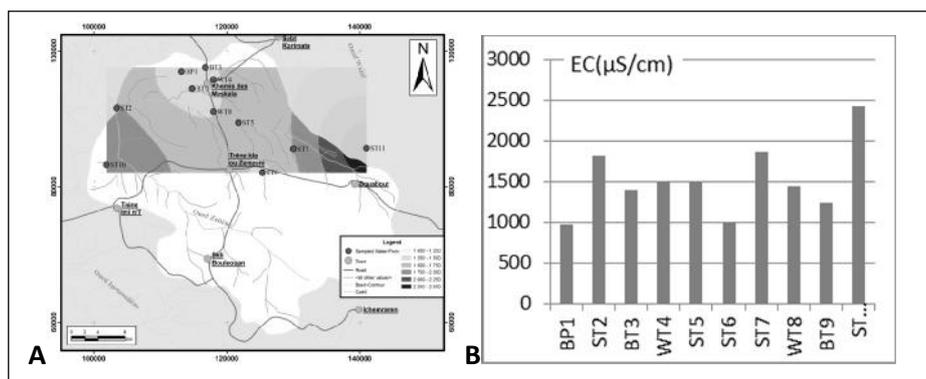
Figure 8: A- Maps of the spatial distribution of electricalconductivity **B-**Values of electrical conductivity.

The hydrogeochemical facies of the groundwater samples from Kourimat basin can be ascribed mainly to the presence of Na^+, Cl^-, SO_4^{2-} and Ca^{2+} related either to the dissolution of evaporitic minerals, dispersed in the geological layers, formed by evaporation of salt-ladenwater and/orby dissolution of evaporite formations. While the presence of Ca^{2+}, Mg^{2+} and HCO_3^- in the aqueous facies are mostly related to the dissolution of carbonates.

Diagram (Figure 9) reveals the impact of geology on water quality; it also allows to estimate the percentages of chemical elements and their classification.

Comparing the plot distribution of the groundwater samples within the Piper Diagram and the piezometric map a trend can be observed from E towards W (coast line) where the groundwater geochemistry is changing from a Ca-Mg-HCO_3-Cl type to a Na-Ca-Cl-HCO_3type. The "increase" in the Cl content is simultaneous with the growing in Na and K in the groundwater samples, indicating that most probably this trend is associated with dissolution of

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evaporitic minerals. On the other hand, being Kourimat area, sedimentary basin heterogeneities can be found inside the aquifer layers, the deviation of the water sample BP1 can be due to minor contribution of the Triassic formations and the groundwater along the flow path is preferentially dissolving carbonates.

In the diagram anions, there are water points that are virtually one group close to the chlorinated pole (WT4, BT3, ST2...) except the water BP1 point which is close to the pole bicarbonate.

Springs represented in the middle of the triangle do not exhibit dominance. The spatial distribution of these chemicals depend the facies lithological nature of the aquifer and recharge conditions. Indeed, the abundance of Triassic salt formations on the east and west boundaries and layers of limestone crust in the aquifer is in perfect agreement with the chemical facies water.
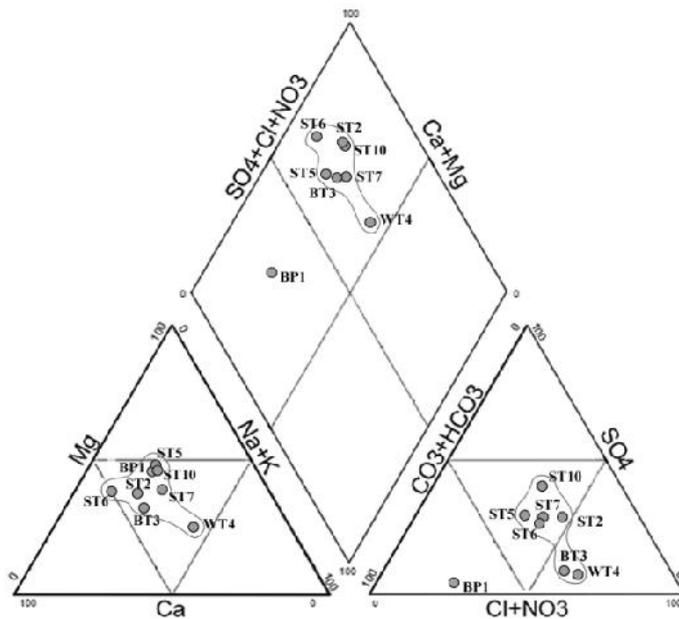
Figure 9: Piper diagram showing the composition of Ceno-Turonian groundwater in the study area.

To understand the process of mineralization of groundwater, we represented major ions as a function of chloride content (Figure 10).For most case studies Cl^- not participating in water-rock interactions processes, being mostly ascribed to the origin of the water salinity behaving as a tracer blend. The arrangement of the various points of water relative to the analyzed line fresh and salt-water mixture (rainwater, seawater) can be very useful to identify other phenomena which are attached to the mixing process, such as the dissolution of evaporate minerals.

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Groundwater different watering points in general show Ca^{2+} enrichment and depletion of Na^+, K^+ and SO_4^{2-}, while for Mg^{2+} was a dispersion of points around the mixing line. Recognized as responsible enrichment or depletion of elements in ground water exchange reactions are major Ca^{2+}/Mg^{2+} due to the interaction water-carbonate rocks, base exchange Na^+/Ca^{2+} or Na^+/Mg^{2+}, reduction or dissolution of the sulphates.

- The relationship of Cl^- and SO_4^{2-} shows that except for some points of substantially all points is located below the line and showing a mixture enrichment which can be related to the presence of the limits and evaporites in gypsiferous-marl substratum and / or an agricultural contamination. In this region the infiltration of rainfall and irrigation water loaded with salts and fertilizers.
Only one sample ST10 is plotted above the mixing line, and is located along a different flow path, probably with higher percentage of gypsum (pyrite) due to the heterogeneities in the sedimentary layers which could be responsible for the enrichment in SO_4; the high content in Cl observed in the sample WT4 and its content in Na seems to related to evaporatic minerals dissolution.

- The relationship between Mg^{2+} and Cl^- shows enrichment of almost 50% of being analyzed with respect to the right mixing water samples. This enrichment may be due to the dissolution of the dolomite.
Gypsum saturation indices were also modelled with the aid of the PHREEQC-2 program (Parkhurst and Appelo, 1999)..
Water is a solvent of mineral elements and is based on the degree of concentration of each component in three states; balance, undersaturated or saturated with a mineral.
In this context, the identification of the degree of saturation of water will be based on the index value of saturation expressed by the following formula:

$$SI = log (IAP / Ks)$$
With:
SI : The product of the ionic activity of ions.
Ks : The solubility product of the mineral.

When SI = 0, the water is in equilibrium with the mineral. If SI is greater than zero in this case is supersaturated in the contrary case, is undersaturated.
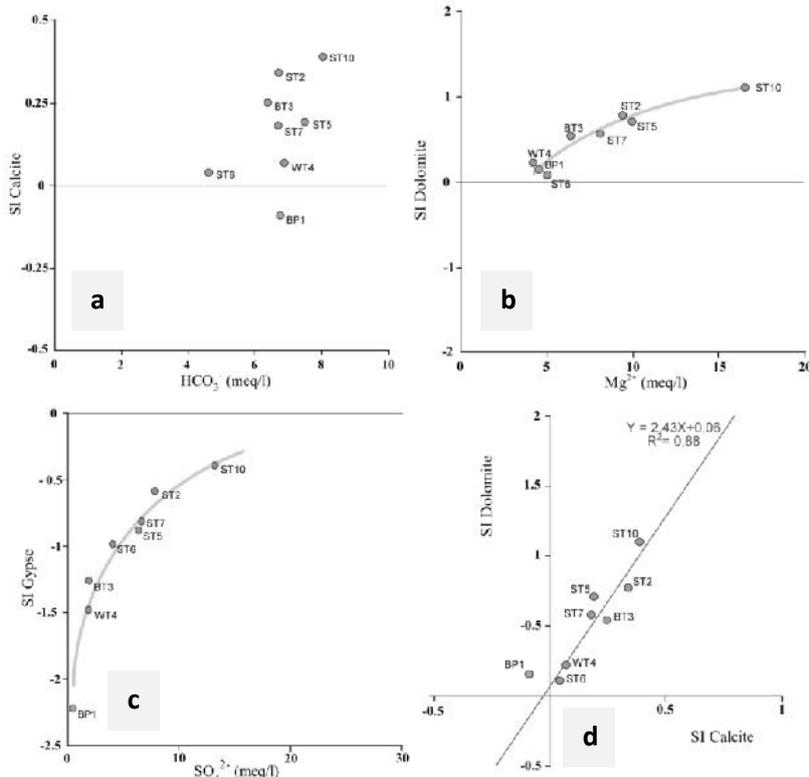
Figure 10: Saturation indices of Calcite (a), Dolomite (b) and Gypsum (c), and versus (Mg$^+$), (HCO$_3^-$), and (SO$_4^{2-}$), respectively, (d) The relationship between saturation indices with respect to calcite and dolomite.

Dissolution of evaporites is also confirmed by the saturation indices They show that almost all samples are undersaturated with gypsum (Figure 10 c).

The relationship between saturation indices with respect to calcite and dolomite of groundwater samples representing the aquifer is presented in (Figure. 10 a, b).

The behaviour of dolomite is quite similar: all samples supersaturated. Ideal conditions for dolomitization are reached. The presence of evaporitic minerals especially hexahydrite explain the increase in Mg$^+$ and SO$_4^{2-}$.

Also we can note the farmers use a type of pesticide that can have Mg$^+$ in their composition

The relationship between saturation indices with respect to calcite and dolomite of groundwater samples representing Ceno-Turonian aquifers is presented (Figure 10 d). The saturation indices cover the range between 0 and 0.5 for calcite and from 0 to 1.2 for dolomite. The data points are distributed along the

straight line $Y= 2.43X+0.06$ ($R^2= 0.88$). Most of the analyzed waters are supersaturated with respect to both carbonate minerals.

- The diagram against Na^+/Cl^- shows that all the points lie below the mixing line. Since the Na^+ content should balance Cl^-, Na^+ deficiency is explained by the base ion exchange phenomenon between the aquifer and the water and resulting in an adsorption of Na^+ and a release Ca^{2+}.

First plot Na versus Ca to see the samples distribution if can found any trend most probably you will see none. Then try to estimate the importance of ion exchange mechanism. The ion exchange mechanisms able to influence the ion concentration of the groundwater through the application of the equation presented by (Pennisi et al., 2006), the magnitude of ion exchange processes for Ca^{2+} and Na^+, was calculated by comparing the difference (n) between the measured concentration ($n_{(m)}$) and that expected by mixing with seawater ($n_{(c)}$), based on the contribution from the conservative ion Cl^- (Pennisi et al., 2006)

The mixing equation for ion X is:

$$\Delta n_x = n_{x(m)} - n_{x(c)}$$

$$\Delta n_x = n_{x(m)} - \left[n_{x(0)} + \left(n_{Cl(m)} - n_{Cl(0)} \right) \left(\frac{n_{x(Sea)}}{n_{Cl(Sea)}} \right) \right]$$
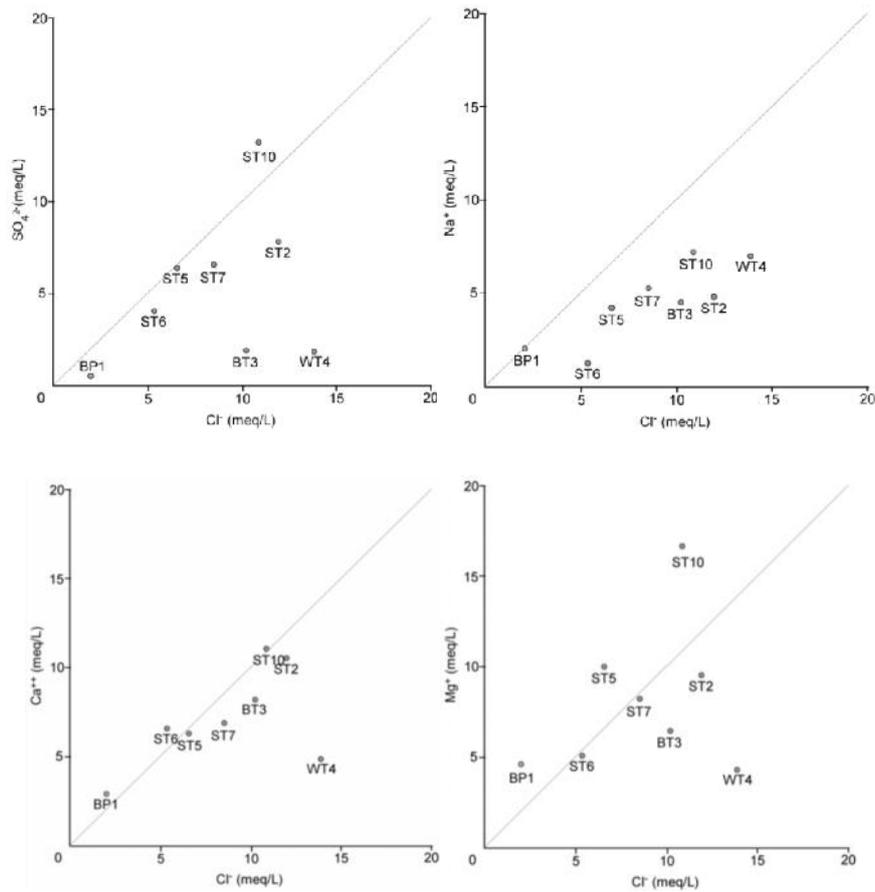
Figure 11: Sulfate, sodium, calcium and magnesium versus chloride for groundwater.

- The relationship between Ca^{2+} and Cl^- illustrates this by showing that the points are frequently above the right mixture of fresh and salt water. Also, we mention the proximity of the samples WT4, BP1 and BT3 in the region, located more or less along the same flow path, and in the diagram are found completely apart each other probably due to the local heterogeneities of the geological formations associated with the possible ion exchange mechanisms.

Table 1: Physico-chemical parameters of groundwater in study area.

Code	C (µS/cm)	T °C	HCO$_3^-$	Cl$^-$	NO$_3^-$	SO$_4^{--}$	Ca^{++}	Mg^{++}	Na$^+$	K$^+$
BP1	966	24.4	411.80	71.80	19.30	22.70	58.40	56.30	47.40	2.2
ST2	1810	29.5	408.70	424.30	22.00	374.80	211.00	115.30	111.20	6.1
BT3	1400	25.8	390.40	362.10	45.30	90.00	163.80	77.70	103.20	4.2
WT4	1500	23.5	420.00	492.20	9.60	89.20	97.60	51.60	160.50	3.3
ST5	1500	22.8	457.50	234.30	38.80	307.90	126.10	121.00	96.90	4.5
ST6	1008	22.9	283.70	189.60	39.60	195.40	130.60	61.50	29.10	4.3
ST7	1867	20.0	409.00	301.90	35.70	314.50	137.10	99.10	121.60	13.6
WT8	1450	24.4	-	-	-	-	-	-	-	-
BT9	1232	24.6	-	-	-	-	-	-	-	-
ST10	2430	20.0	490.40	385.60	16.90	635.70	220.60	201.60	164.80	6.6

Isotopic results

The diagram Cl vs. ^{18}O at the first moment it seems that no correlation or a weak correlation between these two parameters is occurring, pointing, in this case, the salt dissolution diaper structure, since no strong isotopic enrichment is observed (the samples are plotted along the GMWL) no reflecting a mixing with a different type of water with much higher Salinization.
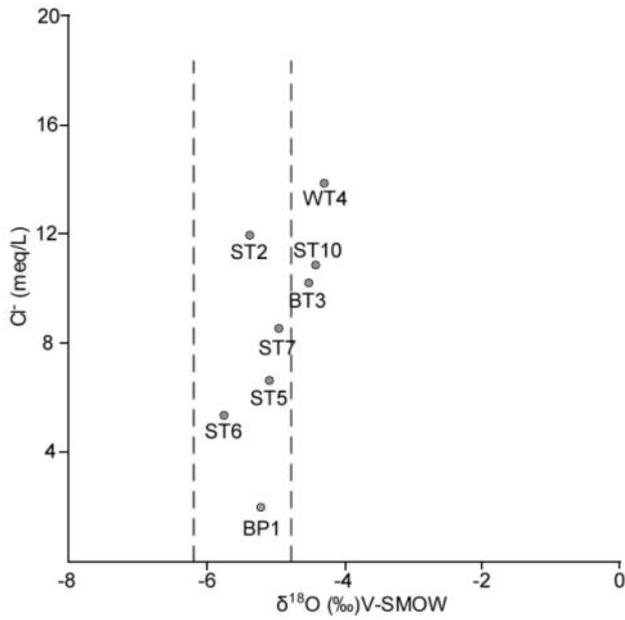
Figure 12 : Cl⁻ (meq/L) / ¹⁸O (‰) diagram of the groundwater.
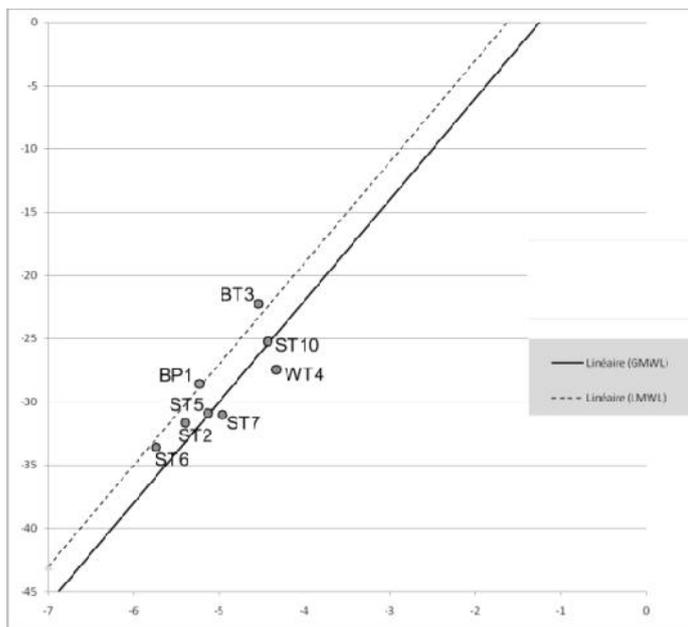
Figure 13: Relationship between ¹⁸O (‰) and ²H (‰) for ground water in the study area.

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It doesn't look that all these samples belonging all of the same hydrological system. The isotopic results (^{18}O) shows a difference higher than 1 ‰ in ^{18}O, this isotopic different can be ascribed to different recharge altitudes.

The electrical conductivity values (Table 2) and plot the EC versus the isotopic composition. Using a different scale (^{18}O from -7‰ to -3 ‰) a small coefficient correlation is obtained (r =0.54). This can be explained by the presence of two water bodies in Ceno-Turonian aquifer.

Regarding the ^{14}C and ^{13}C data, it seems that the source of carbon is all the same (dissolution of carbonate layers along the flow) the isotopic signal from the soil zone (organic carbon (CO^2) associated to the roots of plants respiration) is not visible.
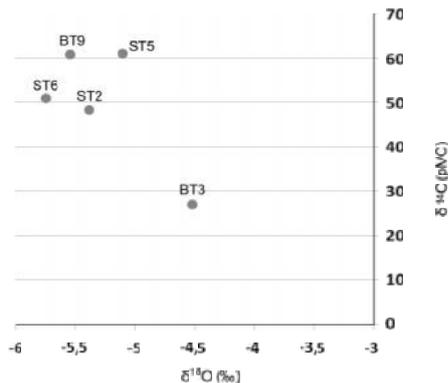
Figure 14: ^{14}C (pMC) / ^{18}O (‰) diagram of the groundwater.

From the diagram ^{14}C versus ^{18}O its showing the presence of a climatic signal reflected in the oxygen-18 data, same recharge area and soon. However, using a simple model to calculate the apparent carbon-14 groundwater ages the values obtained are presented in the table 2:

Table 2: Isotopic parameters of groundwater in study area

Nom	C (µS/cm)	T °C	^{18}O (‰)	^{2}H (‰)	H^3 TU	^{14}C (pMC)	^{13}C (‰ PDB)	Age BP
BP1	966	24.4	-5.23	-28.59	0.90	-	-	
ST2	1810	29.5	-5.38	-31.81	1.55	48.26	-8.57	3388
BT3	1400	25.8	-4.52	-22.32	-	27.03	-8.87	8464
WT4	1500	23.5	-4.31	-27.39	-	-	-	
ST5	1500	22.8	-5.10	-30.91	1.50	60.97	-10.29	2967
ST6	1008	22.9	-5.74	-33.67		50.90	-8.20	2582
ST7	1867	20.0	-4.96	-31.00	1.09	-	-	
WT8	1450	24.4	-5.18	-31.13	3.20	-	-	
BT9	1232	24.6	-5.54	-30.59	0.70	60.70	-9.47	2317
ST10	2430	20.0	-4.43	-25.23	0.93	-	-	

CONCLUSION

Combined use of hydrochemistry and isotopic composition of groundwater samples collected in Kourimat basin in oust of Essaouira city Morocco allowed a more detailed insight into the processes controlling chemical composition of groundwater and wide-scale interaction water–rock (Ceno-Turonian matrix) with the dissolved components resulting in particular, reflects the predominance of dissolution of calcareous and dolomitic rocks and corresponds to the majority of wells, the dissolution of evaporites is also confirmed by the saturation indices They show that almost all samples are undersaturated with gypsum.

Overlap of some major characteristics (^{18}O, ^{2}H, Cl^-) in this aquifer indicates that the recharge was carried out under conditions paleoclimatic with the presence of two water bodies coder than the current. It is essentially recharged water from the same altitude. The mixing processes considerably influence the hydrochemical evolution of water, confirmed by a dating done by the carbon 14.

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