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Using Geochemical and Isotope Investigations for Groundwater Management Strategies Under Semi-Arid Area: Case of the Wadi Ouazzi Basin (Morocco)

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Abstract
The characteristics of Essaouira basin water resources are a semi-arid climate, which is severely impacted by the climate (quantity and quality). Considering the importance of the Essaouira aquifer in the groundwater supply of the region, a study was conducted in order to comprehend this aquifer groundwater evolution. The Essaouira aquifer is a coastal aquifers located on the Atlantic coastline, southern (Morocco), corresponding to a sedimentary basin with an area of near 200 km2.A water sampling from twenty wells, drillings and sources belonging to the Plio-quaternary and Tu-ronian aquifers was realized (what was realized). Samples examined from the ground for electric conductivity and temperature, determined waters belonging to the Plio-quaternary and Turonian aquifers present very variable electric conductivities from 900 µs/cm to 3880 µs/cm. In spite of this variability, they form the same family and are characterized by sodium-chloride facies. There exists, however, a good correlation between the electric conductivity and chloride and sodium contents. Therefore the lower electric conductivities are situated in the North quarter immediately in the south of the Wadi Ouazzi.
Keywords: Management, Wadi Ouazzi, Drought, Strategies, Semi-arid, Turonian, Plio-Quaternary.

Introduction:

The countries of North Africa have long had the challenge of providing sustainable livelihoods 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 already 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 involves 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 Essaouira basin is located between Jbel Amsittène in the south and Jbel Hadid in the north. The basin is a vast syncline open to the Atlantic Ocean. The Essaouira basin has a population of 400 000 habitants and is predominantly rural.

The basin area is about 6000 Km^2. the basin is characterized by limited and discontinuous water resources. It is necessary, therefore, to locate potential new areas for groundwater production in order build integrated water supply projects.

Two main aquifers constitute the system. The Mio-Plio-Quaternary aquifer provides the bulk of the water supply and is mainly composed of sand, sandstone and conglomerates. The Cenomanian-Turonian aquifer is mainly Calco-dolomitic. The Cenomanian was recently drilled for supply for the city of Essaouira.

The objective of this study was the application of chemical and isotopic techniques to determine the possible interconnections between aquifers in the coastal zone of Essaouira (Plio-quaternary aquifer) and the aquifers in the Meskala region (Turonian aquifer); quantify mixing between the different aquifers within the Meskala region; and date groundwaters in the coastal zone and Meskala region aquifers.

The value of water is composed of the economic and intrinsic value. The economic value includes not only the value of water to users, but also, the net benefits of return flows (recharge of groundwater), the net benefits from indirect use (improvement in health), and adjustment for societal objectives (poverty alleviation, employment generation). Similarly, water pricing should reflect the scarcity of water. The recommended approach would be to define the water basis of the full cost of supply, it includes operating and management cost, capital charges, opportunity cost, economic and environmental externalities.

Nevertheless, in most countries, water is priced below its full cost. Such pricing system not only underestimates the price of water, it also fails to provide incentives for more efficient water use.

The problem is intensified in coastal aquifers, where human activities result in accelerating water-quality deterioration in particularly in arid and semi-arid areas, the Basin of Essaouira is part of this areas, located in coastal area about 300 Km in south-west of Casablanca in west of Morocco, Africa.

Stalinization of groundwater resources is one the most widespread processes that degrades water-quality and endangers future water exploitation in coastal areas in particular in arid and semi-arid regions.

Drinking water supplying the Essaouira city and its neighboring rural agglomerations is presently based on exploiting underground waters, notably those of the Plio-Quaternary aquifer. This aquifer is submitted to several constraints. Less deep, this aquifer is sensitive to drought episodes, more frequent in Morocco; the most severe one was happened in 1995. It has been shown by this study that the recharge rate of the deep Turonian aquifer is too low. This may cause a lack of water for supplying the Essaouira city and its region.

One of the objectives of this paper is to provide a better understanding of mechanisms that contribute to groundwater mineralization in Essaouira basin and to assist decision makers to prepare scenarios for water management in this watershed.

The water balance of the Essaouira aquifers is irregular, because of the high climatic variability, but in recent decades, this balance has become in continuous deficit, due to the overexploitation of this aquifer, especially in its downstream part.

The balance deficit predictable was already reached, due to combined effect of drought and aquifer overexploitation. The rain water storage in excess periods allows regulating the temporal disproportion between the differences in water demand and those of its availability, pre-venting loss of water to the ocean, to avoid risk due to evaporation of water storage in reservoirs, to alleviate piezometric decreases and improve water quality.

Many studies (Bahir, M., Jalal, M., Mennani, A., Fekri, A.) were concerned with the whole Essaouira basin watershed and the summarized studies of the watershed. The studies demonstrated the mechanisms causing degradation of water quality in some areas of this watershed using the chemical and isotopic tools. They have also shown that most of the natural recharge in the watershed of Essaouira basin comes from the High Atlas, which receives a significant rainfall, especially in its upstream part. This article is a part of the broader issue of water in arid regions.

It comes in addition to these studies. The originality is that it is particularly focused on studying in this part of the aquifer, which represents a recharge area, given to the high permeability and soil structure and the good quality waters in the upstream part of the watershed; to study the quality and renewal of water resources in this semi-arid region.

1. Study area

1.1. Geographical context

The study area is located in the upper zone of the Essaouira basin. It is bounded in the Ouest by Wadi Mramer basin, in the north by Igrounzar Wadi crystalline massive in the east.

1.2. Climate context

The rainfall presents a large spatial and temporal variability from 400 to 560 mm in the High Atlas to approximately 280 mm/yr in the plain. The average of potential evaporation ranges from 780 mm in the mountains and near the Atlantic coast to 920 mm in the plain.

In the study area severe and widespread dry conditions occurred, especially in 1998, 1999 and 2000 (Figure. 2). The decrease of winter precipitation may have resulted in a degradation of the soil moisture content and a depletion of the ground water level.

The climatic pattern in this area is frequently characterized by a relatively "cool" dry season, followed by a relatively "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.

1.3. Geology and hydrogeology

In geological terms, the Essaouira synclinal zone is less rugged, with a lower relief (Figure. 1), characterized by low hills and shaped by a sparse water system. The Plio-Quaternary and Turonian are the main reservoirs of groundwater in the Essaouira Basin. The Plio-Quaternary, with a matrix of sandstone or limestone marine dune has a hydraulic conductivity primary porosity and contains a large free surface whose wall is formed in the synclinal structure, by the Senonian marls, flayed the ante-Pliocene shows that the Plio-Quaternary can be in direct contact with the Triassic and Cretaceous other levels (Laz, 1959; SCP, 1959). It is operated in rural areas and provides drinking water, domestic needs and a lesser extent irrigate farmland (Bahir et al. 2000).

There are two main aquifers:

The main karstic aquifer is contained within Cenomanian and Turonian limestones and dolomitic limestones. The base of the system corresponds to lower Cenomanian grey clays and the top to the Senonian white marls (Figure. 4). The structure of the basin is marked by a succession of anticlines and synclines, affected by folded structures and deep faults (Figure. 5, 6) under the influence of Atlas tectonic and Triassic salt diapirs.

The Plio-Quaternary aquifer consists of sands, sandstone and conglomerates and provides the main part of the water supply.

2. Method and materials

2.1. Sampling and analyses

Especially the wadi Ouazzi (20 samples) at the coast, springs and water samples spreading out to the Upstream (wells and boreholes). Sampling localities are shown in (Figure. 7). 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, and other ions (Ca^{2+}, Mg^{2+} ,Na^{+}, K^{+}, Cl^{-}, SO_4^{2-},NO^3) laboratory at the University of Marrakech (Morocco).

The stable isotope analyses (20 Isotopic analysis), δ^2H (‰), $\delta^{18}O$ (‰ VSMOW) and $\delta^{13}C$ (‰ VPDB), were performed by mass spectrometry and the radiocarbon (^{14}C) analyses reported as percentage modern carbon (pMC) were per-formed in both laboratories of AIEA.

2.2. Methodology

For this study 20 groundwater and surface water sampling points were chosen (Figure. 1, Table 1). They represent hydrochemical types of water and hydrogeological conditions typical of different sectors of the Plio-Quaternary and Turonian aquifers. The measurements of water temperature, pH, Electrical Conductivity (EC) and total alkalinity were carried out on-site. Analyses of major ions and isotopic composition ($\delta^{18}O$ and δ^2H of water, $\delta^{13}C$ and ^{14}C content of TDIC reservoir) have been performed on all samples.

Stable isotope composition of water samples ($\delta^{18}O$, δ^2H) was determined at the Laboratory by Laser spectrometry measurement. The results are expressed as relative deviations δ (in per mil) from the Vienna Standard Mean Ocean Water (VSMOW). The analytical precision of stable isotope analyses (1σ) was in the order of 0.1‰ for $\delta^{18}O$ and 1‰ for δ^2H.

Evaluation of the groundwater data was carried out by statistical methods, and afterwards, geochemical and isotopic methods were made to establish the processes controlling the groundwater chemistry. 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).

This hierarchical clustering was developed using a combination of the Ward's linkage method (Ward, 1963) and squared Euclidean distances as a measure of dissimilarity. Finally, it produces 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. The aim of PCA is 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).

Also, stable isotopes (deuterium ^2H and oxygen ^{18}O) have been used as an integral component of hydrogeological and geochemical methods in order to identify possible recharge processes, mechanism of salinization of groundwater and mixing within aquifer systems (Fontes, 1980; Rozanski, 1985; Edmunds et al., 1992; Clark and Fritz 1997).

3. Results and discussion

3.1. Results

The groundwater Plio-Quaternary and Turonian is characterized by their hydrochemical variability. Indeed, the recorded conductivity varies from 900 ms cm^{-1} to more than 3,500 ms cm^{-1} (Figure. 8), with an average of 2,000 ms cm^{-1}.

3.2. Geochemical processes

Usually, major ions studies are used to define hydrochemical facies of waters and the spatial variability can provide insight into aquifer heterogeneity and connectivity (Murray, 1996; Rosen and Jones, 1998).

A general evolution of major ions concentrations, EC and TDS displays an increase in mineralization when going upstream towards the medium part of the plain.

Piper diagram (Figure. 11) allows a global visualization of the chemical water types while identifying potential chemical evolutions.

In the major cations triangle, groundwater samples are almost, totally located close to the (Ca^{2+} Mg^{2+}) poles. In fact, Ca^{2+} represents 40% of the sum of major cations; Mg^{2+} represents 70%, and Na^{+} 20%. On the other hand, surface waters are more enriched in sodium, Ca^{2+} represents 35%, the (Na^{+}, K^{+}) and Mg^{2+} concentrations are 35%

and 21%, respectively, due to their crystal-line origin.
In the major anions triangle, waters are mainly located in the bicarbonate pole with a migration toward the sulfate pole. HCO_3^- is dominant with 52% of the sum of anions for groundwater; the SO_4^{2-} and Cl^- are secondary represents 16% and 60%, respectively. For surface waters, HCO_3^- is also dominant with 56%; SO_4^{2-} and Cl^- represent 15 % and 11%, respectively. The water samples situated in the center correspond generally to waters from basement. In the Cl^-+NO_3^- pole, it is necessary to distinguish the salinity caused by Cl^- concentration and the pollution caused by nitrates.
Even with this variability, the waters of the groundwater are grouped in one family and are characterized by the sodium-chloride facies (Figure. 12).
The analysis of maps of the spatial distribution of sodium (Figure. 18 **A**), chlorides (Figure. 18 **B**) and electrical conductivity show that there is a good correlation between the concentrations of chloride and sodium and that the distribution of these two factors correlate well with the electrical conductivity. Examination of the spatial distribution map of mineralization of water (Figure. 18) shows some chemical zonation mainly due to the lithological nature of land crossed. We have the lowest electrical conductivity; they increase fairly steadily to the northwest, with a maximum near the Bouzerektoun in the West.
If the intensification of agriculture through irrigation in the basin of Wadi Ouazzi helped quickly and significantly to the increase in agricultural production, it is responsible for its share of diffuse pollution and deterioration some parameters of water quality.
In general sampling points Basin Wad Ouazzi are characterized by high values of nitrates (see table).
In this area we mainly retain the pesticides and fertilizers. Among the chemicals used in agriculture are cited, inorganic nitrogen compounds that are essential for plant growth.
After erosion and leaching from agricultural land, courses and reservoirs are enriched in nitrates and phosphates. The immediate consequence of these releases is eutrophication.
The sampling point Nguia 612/43 is characterized by a high concentration of nitrates, something that can only be explained by the agglomeration of the surrounding population is mainly by the impact of wastewater that is discharged through septic tanks (Figure. 18 C).

3.3. Isotope results

The interpretation of Oxygen and Hydrogen isotope data allows the two Plio-Quaternary and Turonian aquifers to be distinguished, which was not obvious using major element interpretations.
The value of Plio-Quaternary water lies generally between -3.82 ‰ and -5.88 ‰ if 1699/52 Borehole, which is breached by salted bevel, is excluded from them. The 6180 values for Turonian water lies between -4.71 ‰ and -5.43‰ and are mainly concentrated around the lower value of -5‰.
This difference persists despite the perceptible seasonal variations of the Plio-Quaternary aquifer. It may be related to the difference in altitude of recharge areas.
Turonian horizons are between 400 and 700 m in altitude on the outcrops of the Jbel Kchoula, whereas the average altitude of Plio-Quaternary is between 300 m and sea level.
The results of the ^{2}H isotope analyses, the local meteoric line: $^{2}H = 7.95 \times {}^{18}O + 11.3$ (n = 11, r = 0,97) parallel to the meteoric water line (MWL): 6,2 H = 8,6 × ^{18}O + 10 (Craig, 1961). This line characterizes the oceanic precipitation.
Stable isotope ratios for the sampling sites is practically fixed cluster on or near the global meteoric water line for the Plio-Quaternary and Turonian aquifers, with range from -25 to -40 $\delta\,^{2}H$ (‰)and from -4.2 to -6,22 $\delta\,^{18}O$ (‰) vs.V-SMOW, suggestive of little evaporation prior to groundwater recharge, suggested by the isotopic deviation from the GMWL . (Figure. 19)
The sampling sites (Figure. 20) clearly showing the correlation between altitude and the ^{18}O values was been founded with increasing values of the isotopic composition of the groundwater depending on the altitude.

4. Conclusion

Water resources management in countries that are already severely water stressed faces new challenges. In addressing this uncertain future it is critical to draw as much strength as possible from the lessons of the past, particularly to ensure that the approach chosen, is coherent and clearly articulated to reflect the varied responsibilities and disciplines involved in successful water resources management. The optimal water allocation for a growing number of competing water management requirements (e.g. agriculture, public consumption, hydro-energy, etc.) under a changing climate system places a heavy burden on water managers.
In this case of Essaouira basin this article showing clearly the importance of systematic collection of information on water resources and their dissemination is essential for comprehending and management of water resources.
In this case isotopic and physicochemical results point to a recent increase of groundwater mineralization. The high conductivity (mineralization) content is mostly ascribed to agricultural zones and seaside coastal surroundings, associated with intense overexploitation of groundwater resources and scarcity of precipitation which characterizes the climate in the arid area.

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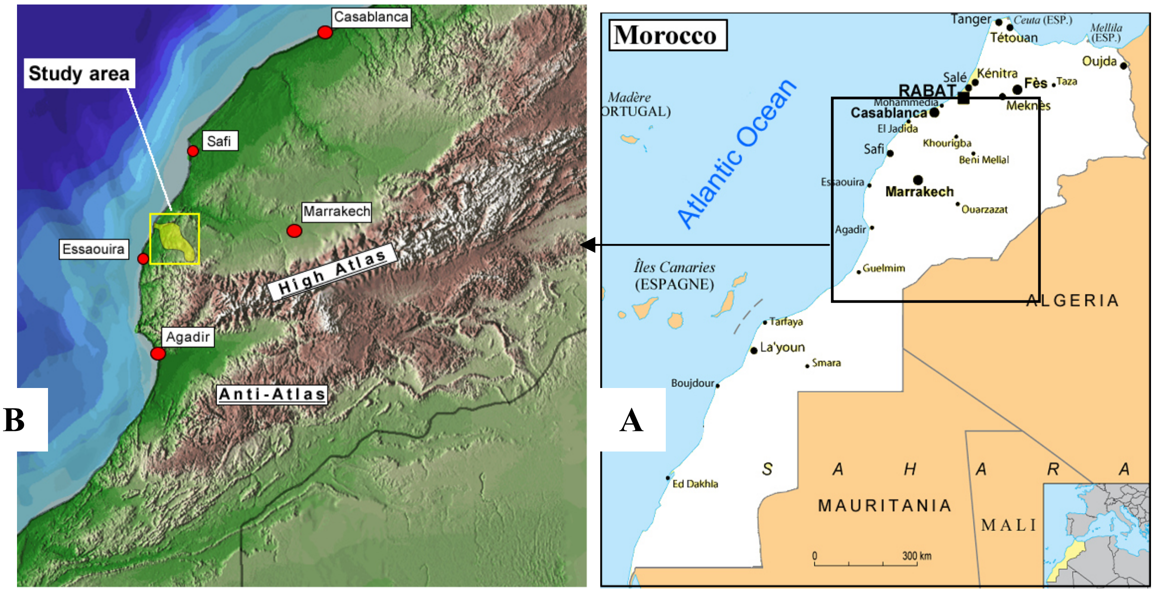
Table1. Physico-chemical and isotopic parameters of groundwater in study area.

Code	pH	C (mS/cm)	T °C	TAC (méq/l)	Depth (m)	HCO_3^-	Cl^-	NO_3^-	SO_4^{--}	Ca^{++}	Mg^{++}	Na^+	K^+	$\delta^{18}O$ (‰)	δ^2H (‰)	H^3 TU	$\delta^{14}C$ (pMC)	$\delta^{13}C$ (‰ PDB)
BT1	6,9	2092	20,8		150,00	305	245,1	38,4	517,2	144,5	123,7	107,6	7,6	-5,39	-31,39	1,25	67,43	-10,44
BT2	7,28	2600	22	6,2	120,00	378,2	634,6	85,8	85,8	150	103,6	167	5,6	-4,71	-26,57	0,42	-	-
WT3	7,24	1500	20	-	15,50	341,6	154,4	49,5	195,2	95,5	83,2	72	2,4	-5,43	-31,42	1,86	-	-
ST4	7,5	998	17,4	5,25	0,00	320,3	100	46,3	23,4	78,5	35,2	68,1	2,9	-5,69	-32,67	3,43	-	-
WT5	7,39	1065	21,9	5,5	40,00	335,5	108,8	39,7	75,2	62,9	55,4	49,9	2,1	-5,68	-33,32	1,69	60,5	-10,82
WT6	7,69	994	21,3	5	53,00	305	68,4	42,8	68,1	72,9	51,3	43,4	2,4	-5,32	-31,57	2,02	-	-
ST7	7,64	3880	17,4	4,4	0,00	268,4	176,4	24,5	2392,5	682	338	56	12,4	-5,43	-34,32	0,43	-	-
WT8	7,6	1600	18,3	6,25	9,25	381,3	165,6	22,3	220,3	71,9	75,5	65,3	4,3	-5,59	-34,23	-	-	-
BT9	7,11	2750	21,5	5,75	110,00	350,8	114,6	26,1	1326,6	358,9	242,5	52,2	8,1	-5,88	-35,71	-	86	-5,12
BT10	7,8	900	23,2		0,00	330	143,7	47,3	176,7	77,7	53,2	119,1	14	-5,29	-29,13	0,18	-	-
WT11	7,10	1900	22,1	5,00	36,00	305,0	1201,7	0,0	7,7	219,9	126,9	193,0	4,6	-5,63	-35,14	1	-	-
ST12	7,65	3740	26,4	-	0,00	142	313,3	24,5	2398,5	578,8	282,7	101,8	10,9	-5,48	-34,26	-	-	-
WT13	7,40	1220	25,0	5,50	170,00	335,5	127,8	0,0	214,9	49,3	52,6	123,6	13,9	-5,25	-29,76	-	-	-
BT14	7	2300	26,2	6,5	152,66	396,5	429,6	12,9	355,2	130,5	139,7	108,9	5,4	-4,9	-28,87	-	-	-
WT15	7,35	2540	24,4	-	13,45	-	497,4	65,1	418,5	233,3	176,1	193,8	7,1	-3,82	-20,69	-	-	-
WP16	6,90	2500	26,6	6,00	35,00	366,0	570,0	76,3	384,2	267,8	159,1	228,3	6,9	-6,21	-38,37	-	60	-7,41
WP17	6,9	2800	22,8		12,50	402,6	561,3	76,5	365,7	212,7	179	231,2	5,6	-4,7	-24,54	-	-	-
SP18	6,75	3100	22,2	5,5	0,00	335,5	841,4	65,3	415,4	255,5	200,4	309,2	4,7	-4,81	-27,57	0,76	74,36	-8,45
SP19	6,65	2700	24,8	7,5	0,00	457,5	610,5	62,9	373,4	188,5	178,2	255,5	4,6	-4,9	-27,89	-	67,65	-9,18
WP20	7,35	2970	22,2	3	45,00	183	667,4	214,1	214,3	300,9	90	255,3	66,3	-4,2	-23,69	-	-	-



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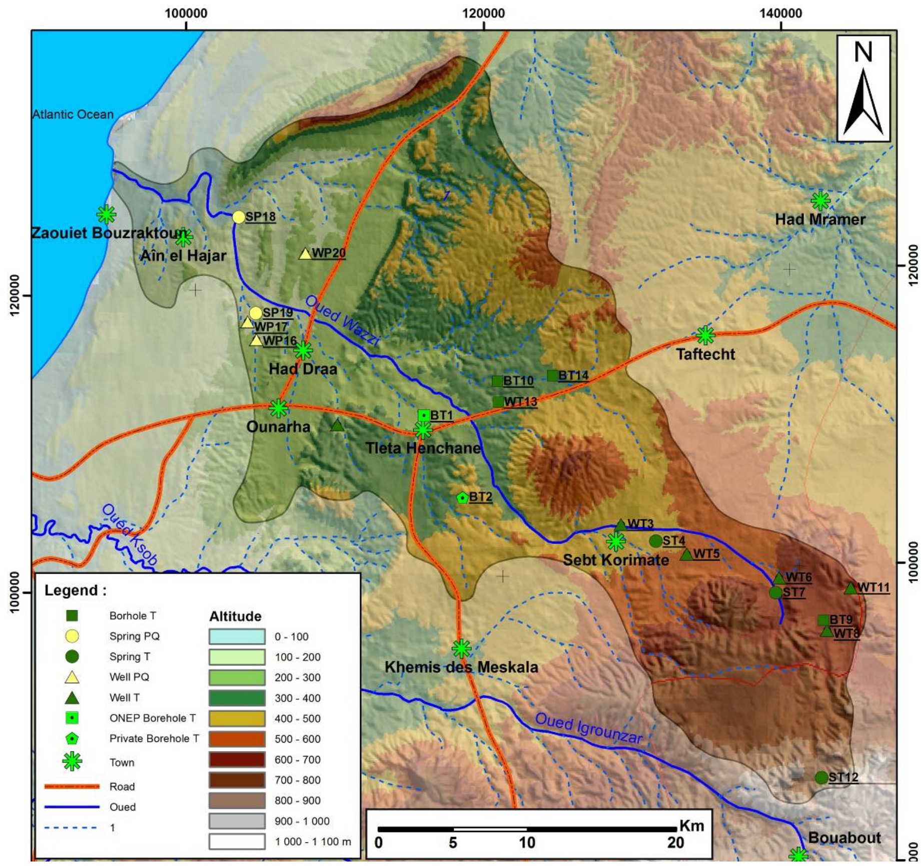


Figure 1. A- Map of Morocco, B- Localization of study area, C-Localization of samples water point in Ouazzi basin.

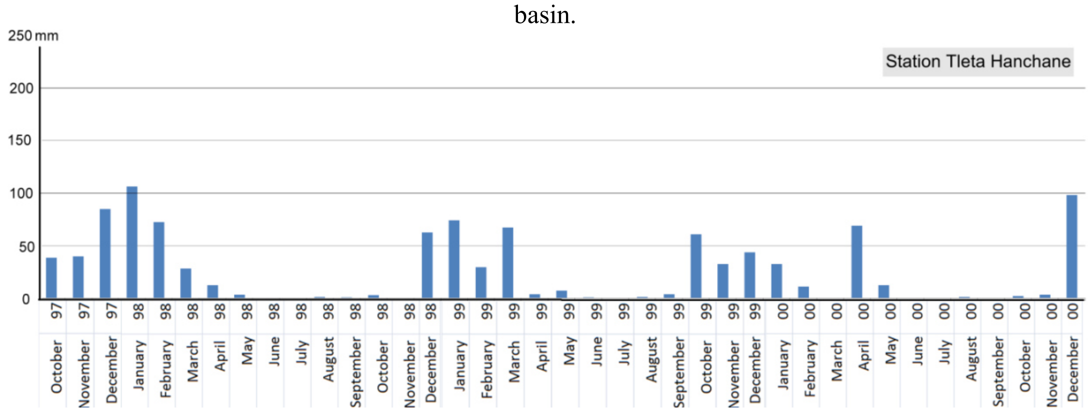


Figure 2. Precipitation annual values and monthly mean values at Tleta Hanchane Station (1997 to 2000).

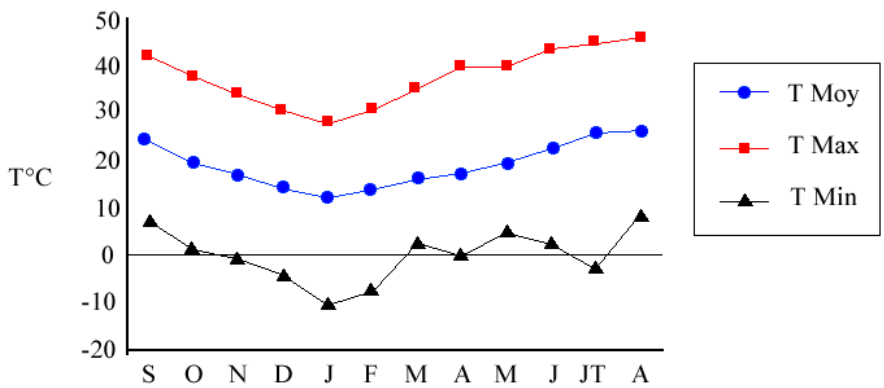


Figure 3. Average temperature per month in Igrounzar station.

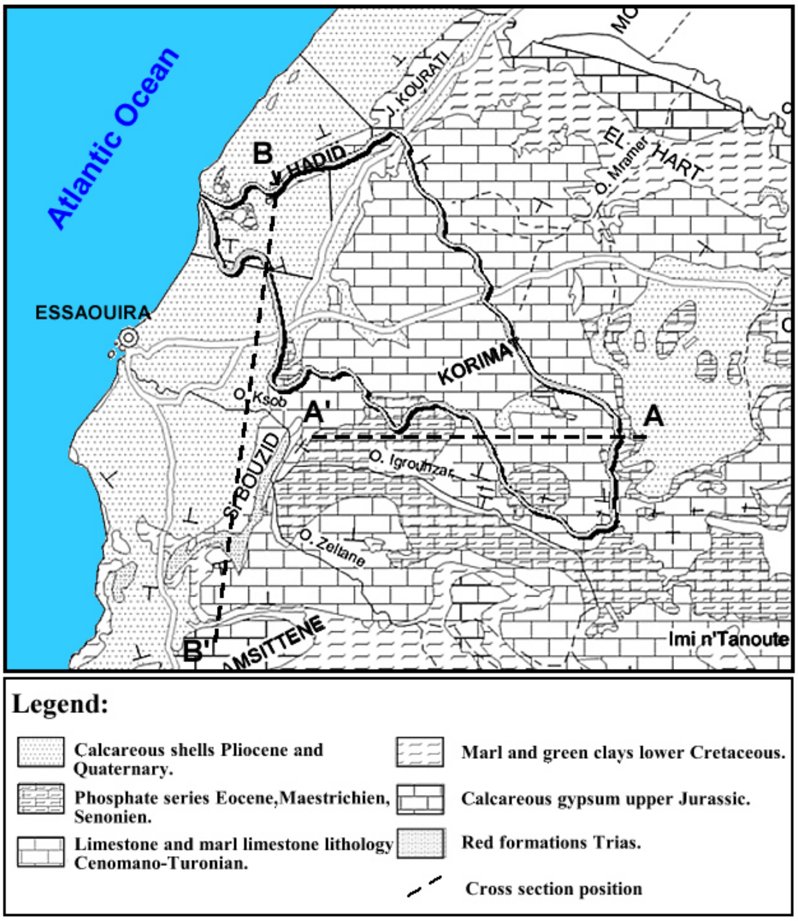


Figure 4. Geological map of study area.

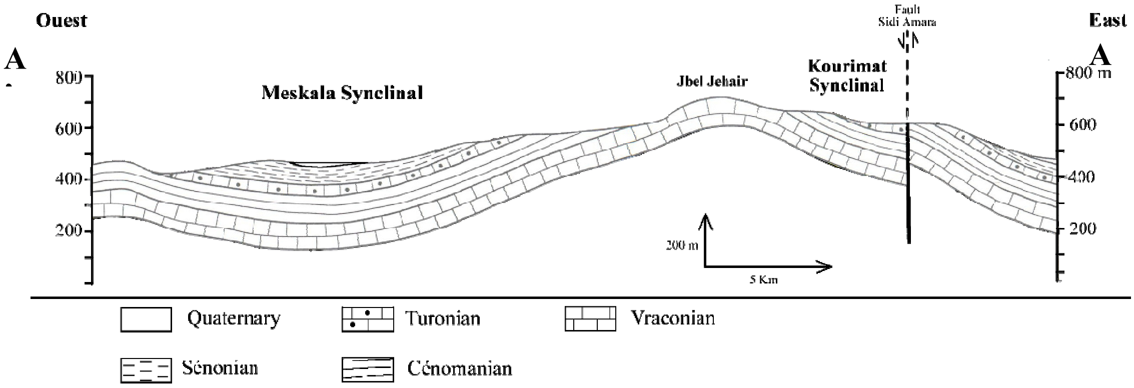


Figure 5. Schematic section showing the geological limits of aquifers in the South-East of Oued Ouazzi Basin.

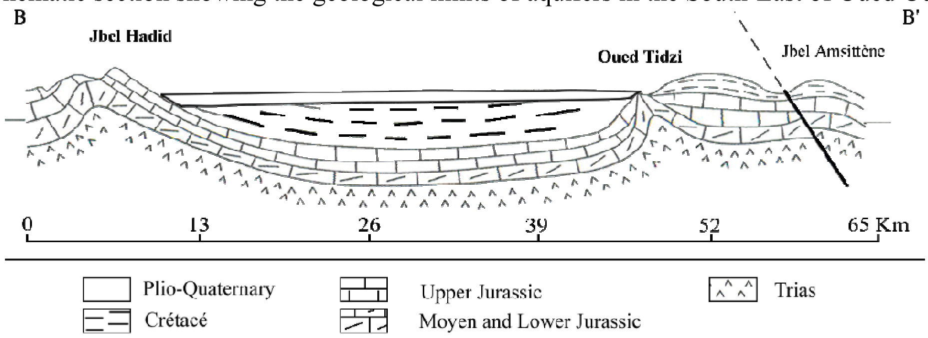


Figure 6. Schematic section showing the geological limits of aquifers post Jurassic (Ambroggin, 1963)

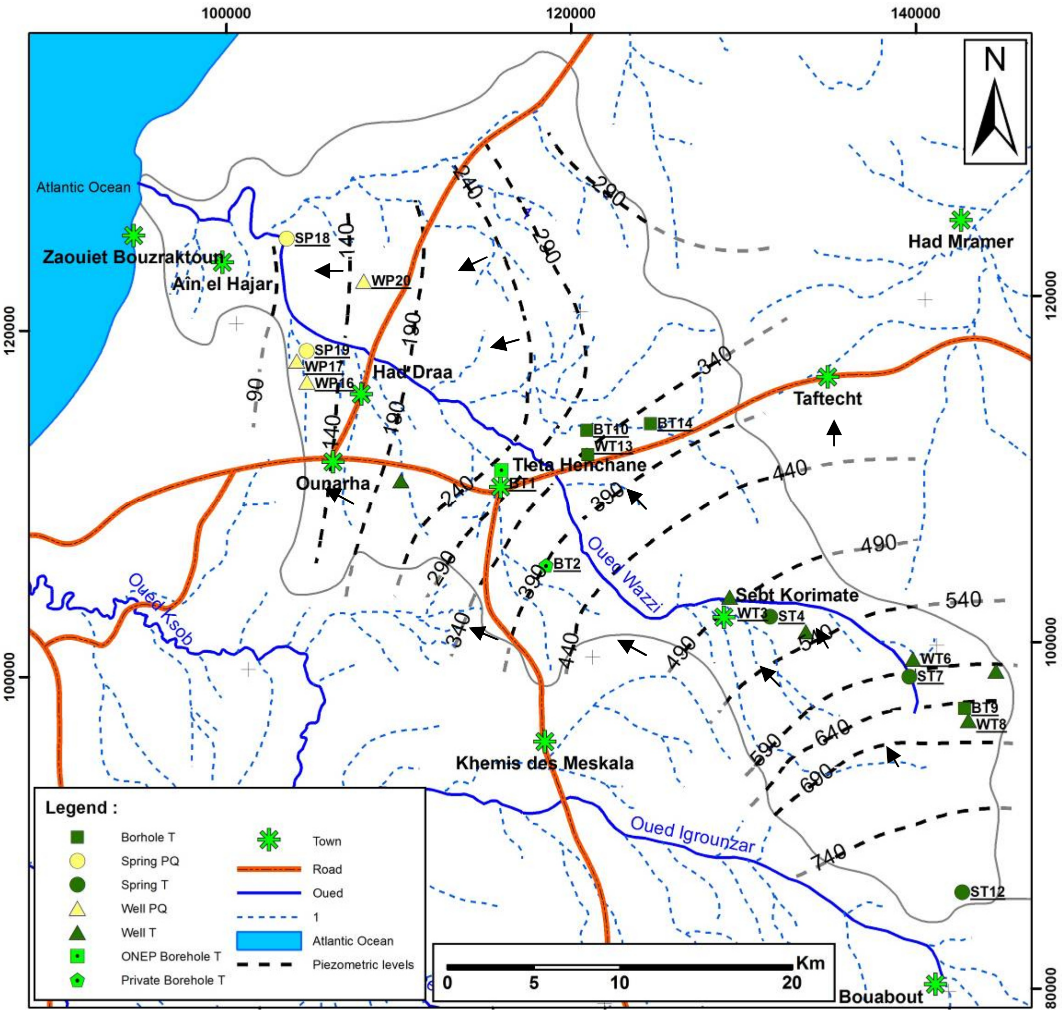


Figure 7. Location of sampled points and piezometric contour map.

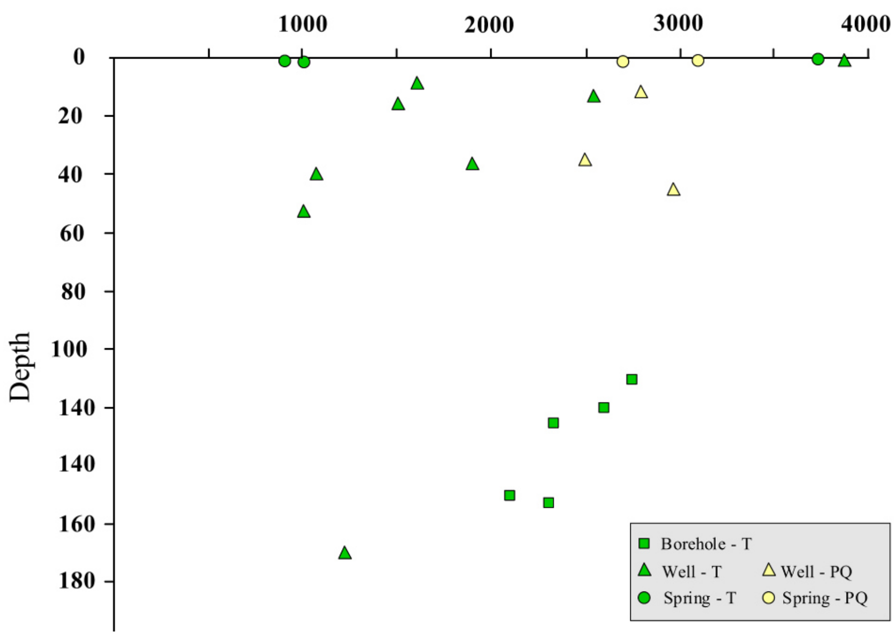


Figure 8. Plot of the electrical conductivity (EC,µS/Cm) and Depth.

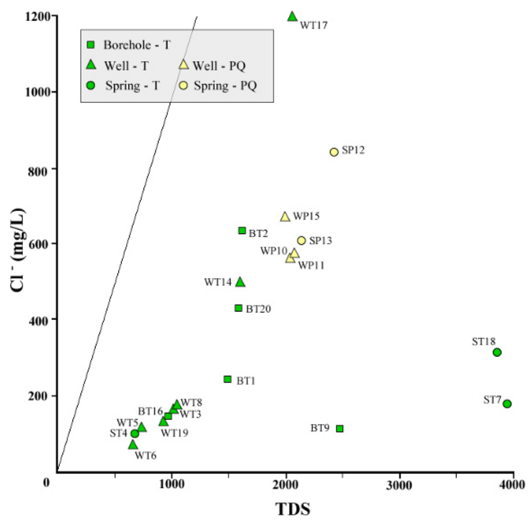


Figure 9. [Cl$^-$]/TDS correlation in groundwater

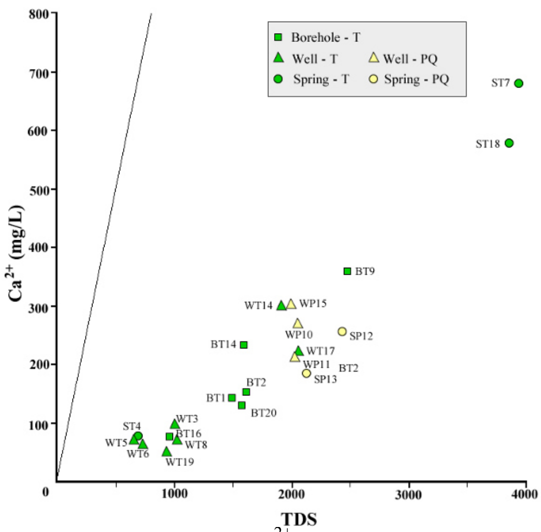


Figure 10. [Ca^{2+}]/TDS correlation in groundwater

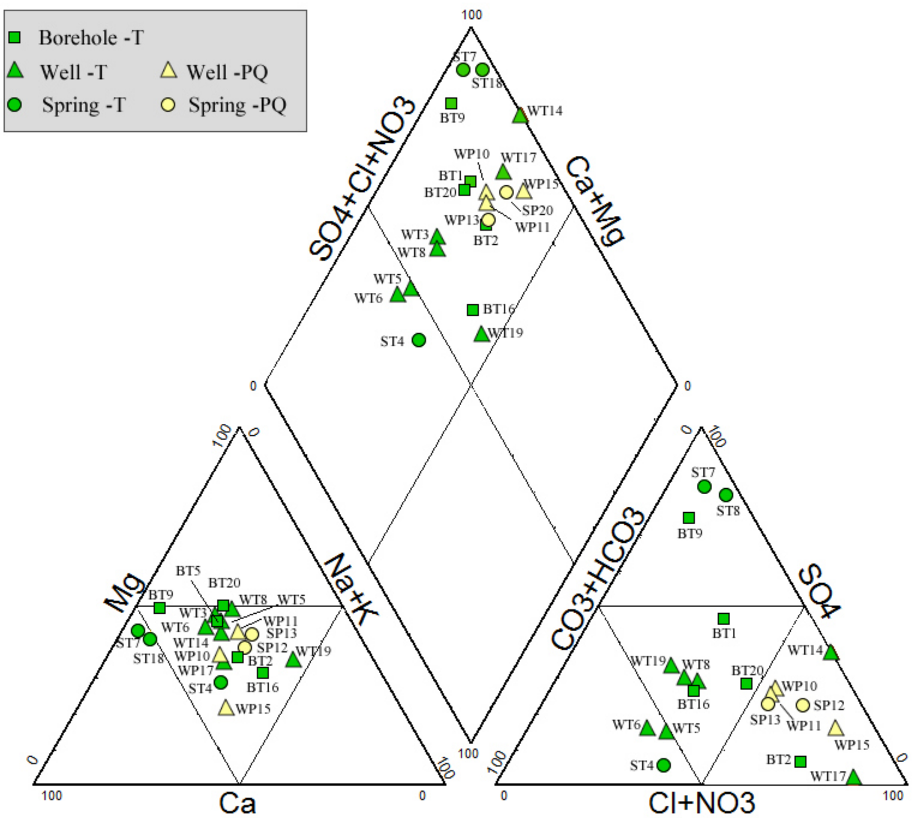


Figure 11. Piper diagram showing the composition of the Plio-quaternary and Turonian groundwater in the study area.

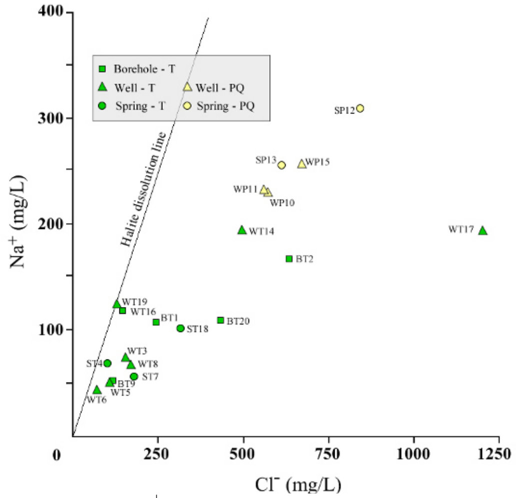


Figure 12. $[Na^{+}]/[Cl^{-}]$ correlation in groundwater

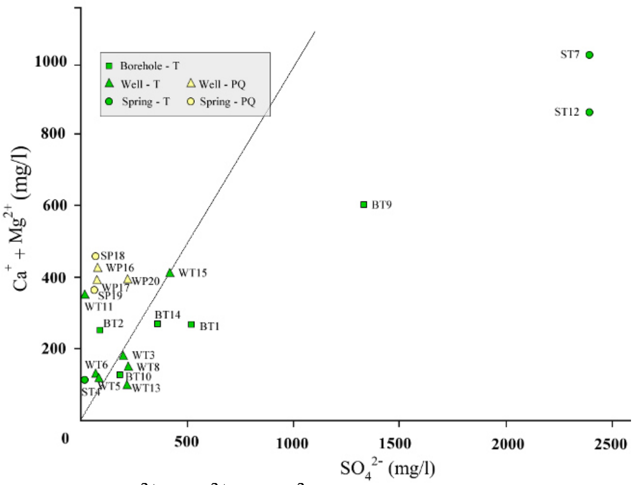


Figure 13. $[Ca^{2+}+Mg^{2+}]/[SO_4^{2-}]$ correlation in the groundwater

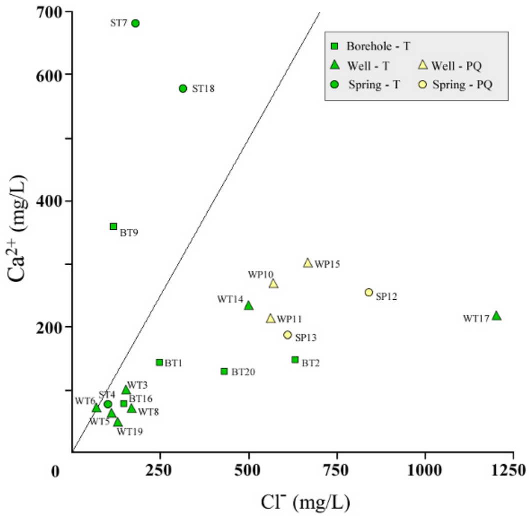


Figure 14. $[Ca^{2+}]/[Cl^{-}]$ correlation in groundwater

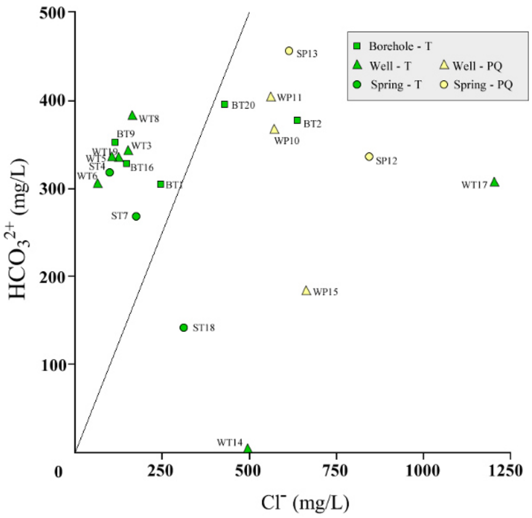


Figure 15. $[HCO_3^{2+}]/[Cl^{-}]$ correlation in groundwater

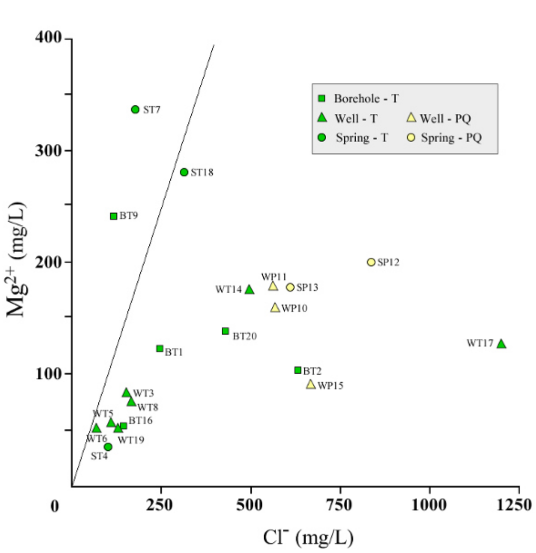


Figure 16. $[Mg^{2+}]/[Cl^{-}]$ correlation in groundwater

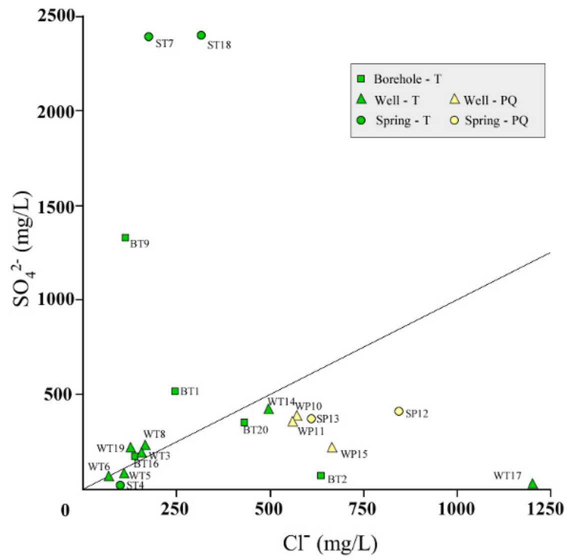
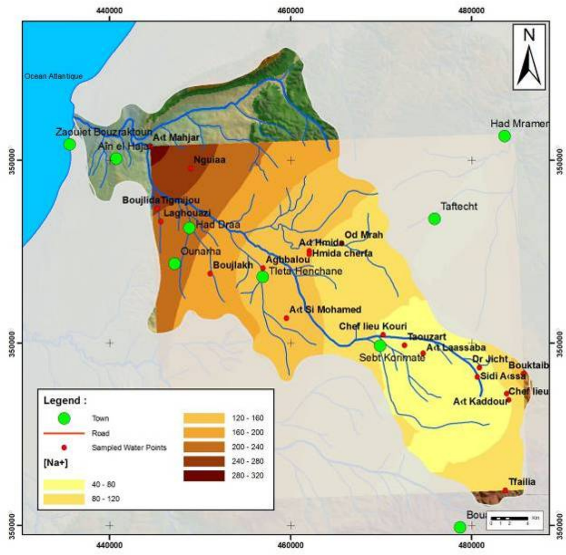
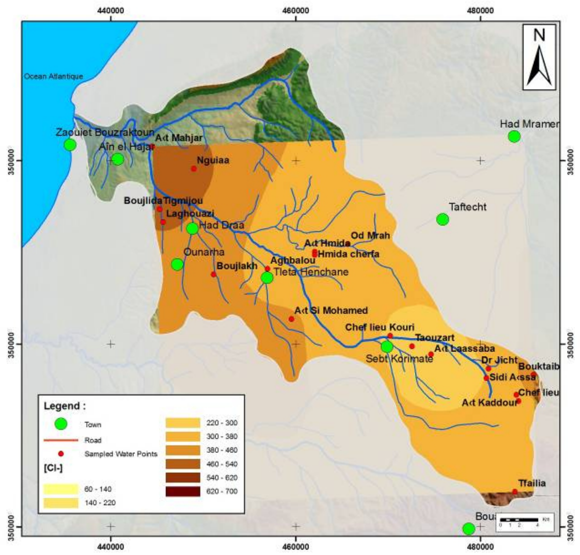


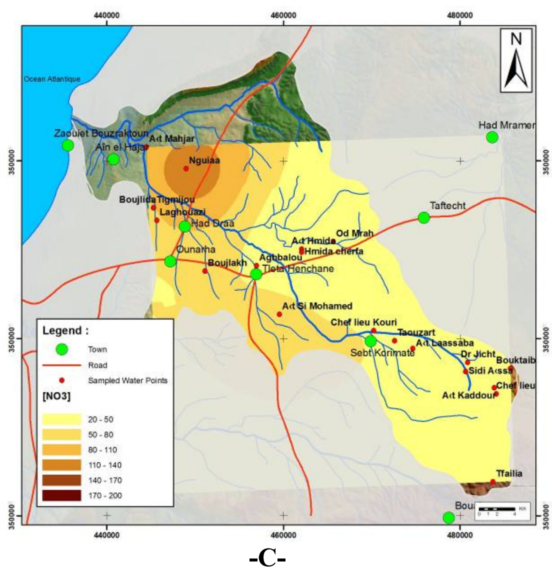
Figure 17. $[SO_4^{2-}]/[Cl^{-}]$ correlation in groundwater



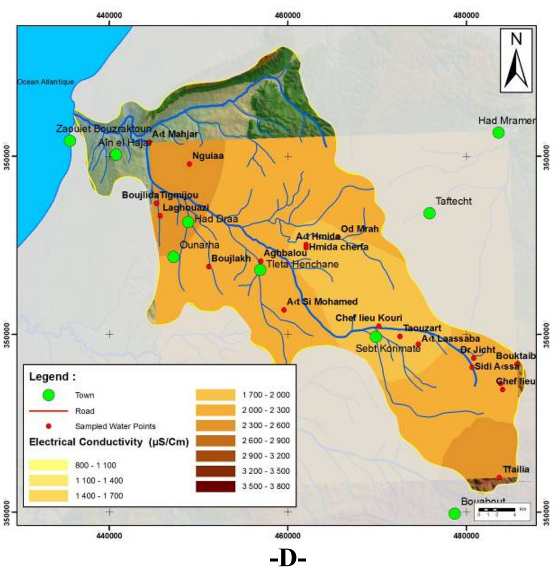
-A-



-B-



-C-



-D-

Figure 18. Maps of the spatial distribution of sodium -**A**-, Chlorides -**B**-, Nitrates - **C**- and Electrical

Conductivity - **D**-.

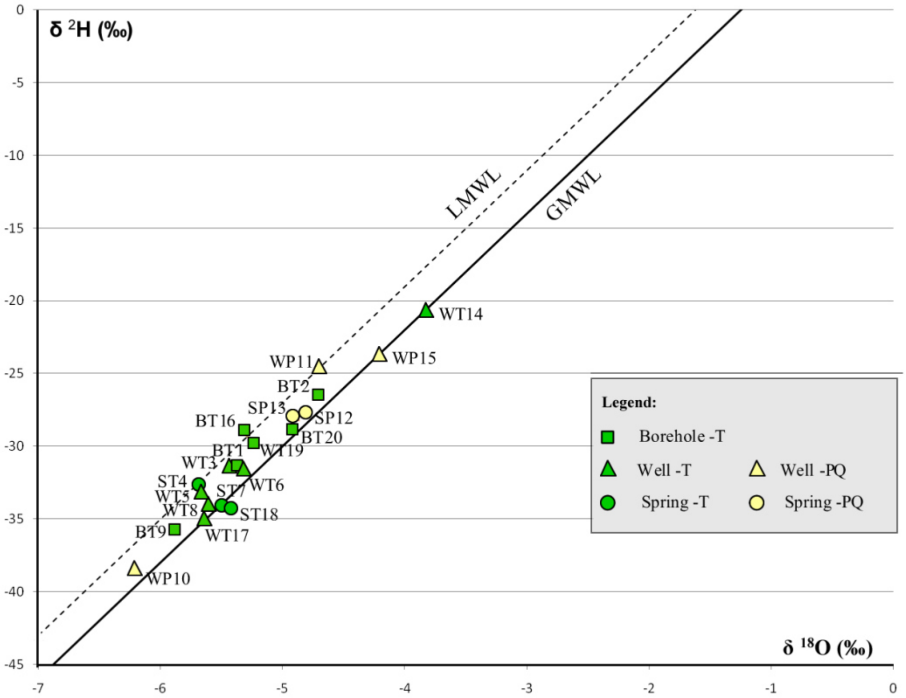


Figure 19. δ ^{2}H (‰) / δ ^{18}O (‰) diagram of the groundwater.

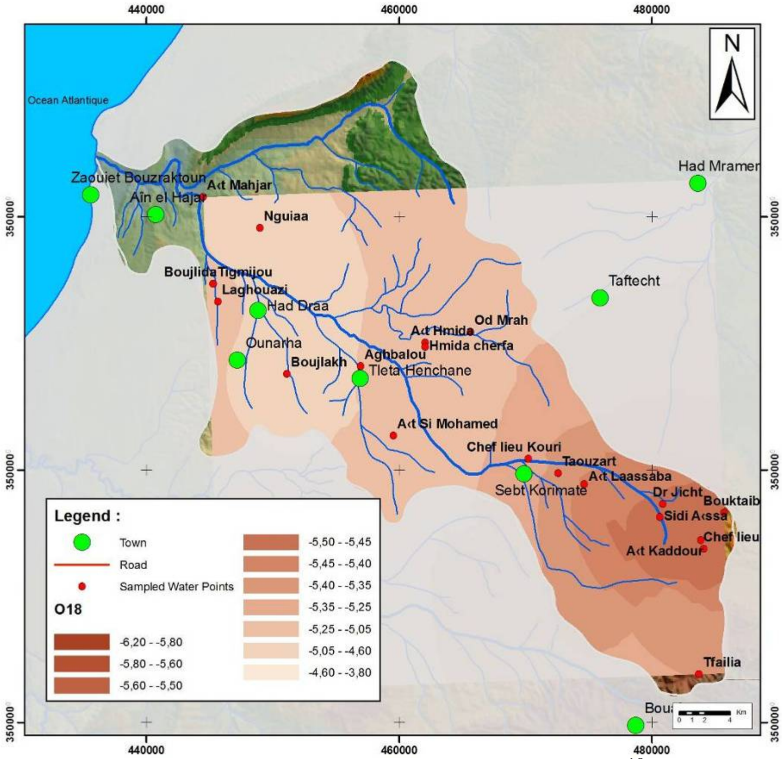


Figure 20. Map showing the regional values of δ^{18}O.