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Physico-chemical quality and origin of groundwater of an aquifer under semi-arid climate. Case of the Barremo-Aptian aquifer of Essaouira basin (Morocco Occidental)

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Abstract
The study area is part of the semi-arid areas of Morocco. It is located about thirty kilometers south of the Essaouira city. It extends between the Tidziwadi to the north and the Amsittene anticline to the south with a surface of 250 km². According to the hydrogeological investigations, the waters of this region is circulating in the formations of Barremian and Aptian age. These are formed of alternating marls, Marno-calcareous to traces of gypsum, limestone fractured fossil and sandstone. Given the importance of this aquifer in the populations supply in drinking water, the study of the water quality is therefore necessary. Of this fact, 26 water points capturing the Barremo-Aptian aquifer were sampled in June 2015 and 3 other in October 2007 for chemical analyzes and isotope. The results of the approach hydrochemical conditions have helped to distinguish between two facies types: Ca-Mg type-Cl representing the downstream part of the aquifer and the type Ca-Mg-HCO_3 governing the upstream part. 50% of the waters from the Barremo-Aptian aquifer displayed an average quality, the rest shows a quality poor to very poor. The bad and very bad quality generally result from the presence of nitrates with concentrations that greatly exceed the standards of potability. The isotopic study shows that the Barremo-Aptien aquifer recharge is ensured by the direct infiltration, without evaporation, of precipitation of oceanic origin. This recharge is performed at an altitude of 600 m asl, to the East of the study area, where are flush with the formations of the Barremian and Aptian. The Barremo-Aptien aquifer presents old waters indicating a low rate of renewal.

1. Introduction
In arid and semi-arid areas, the scarcity of surface water drives local populations to exploit groundwater. Population growth, the expansion of irrigated areas and climate change has greatly increased the pressure on water resources [1, 2]. These are often exploited to the limit of their availability. They then mark considerable piezometric drops and a degradation of their quality by salinization or by contamination. On the Moroccan scale, water availability is very limited and could decrease due to the recurring drought. This halves the renewable water resources making Morocco in chronic water stress [3].

The Essaouira basin is one of the coastal basins of Morocco. It is very vulnerable to the development of anthropogenic activities and climate change in addition to the phenomenon of marine intrusion [4-10]. This sedimentary basin is a set of synclines, which makes it the seat of several aquifers. Among them, the Barremo-Aptian aquifer, object of this study.

The present study attempts to evaluate the physicochemical quality of groundwater and to determine the recharge areas of the Barremo-Aptian aquifer of the Essaouira basin, through the hydrogeochemical and isotopic approach.

2. General framework
The Barremo-Aptian aquifer is one of the main aquifers in the Essaouira basin. It is located about thirty kilometers south of the Essaouira city between Tidziwadi to the north and the Amsittene anticline to the south (Figure 1). This aquifer covers an area of 250 km².

The study area is characterized by a semi-arid climate with an average annual rainfall of 300 mm and an average annual temperature of 20 °C. The climate of the region is marked by an irregular rainfall and a significant water deficit. As a result, the feeding of the Barremo-Aptian aquifer is very variable in time and space and is ensured by the infiltration of water from temporary watercourses.

From a geological point of view, the Essaouira basin is characterized by the outcrop of marine facies (carbonate and marl) representing the Jurassic and Cretaceous, and continental deposits (sandstone and conglomerates) attributed to the Plio-quaternary. The Triassic is marked by saliferous red clays with doleritic basalt passages (Figure 3) [12, 14].

On the hydrogeological level, groundwater flows in the Barremo-Aptian levels generally composed of an alternation of marls, marl-limestone with traces of gypsum, fractured fossiliferous and lumachelliclimestones and sandstones (Figure 2) [13]. The piezometric data collected during the June 2015 campaign made it possible to draw up the piezometric map of this aquifer (Figure 3). There is an SE-NW-oriented general flow imposed by the north flank of the Amsittene anticline and the uplift of the lower Cretaceous lands of the Eastern part, with a feeding zone, or recharge, located in the East. and Southeast. Groundwater level is located at 340 m asl in upstream part of the study area and 20 m asl in downstream part. The hydraulic gradient varies between 3.30% upstream and 3.15 % downstream.

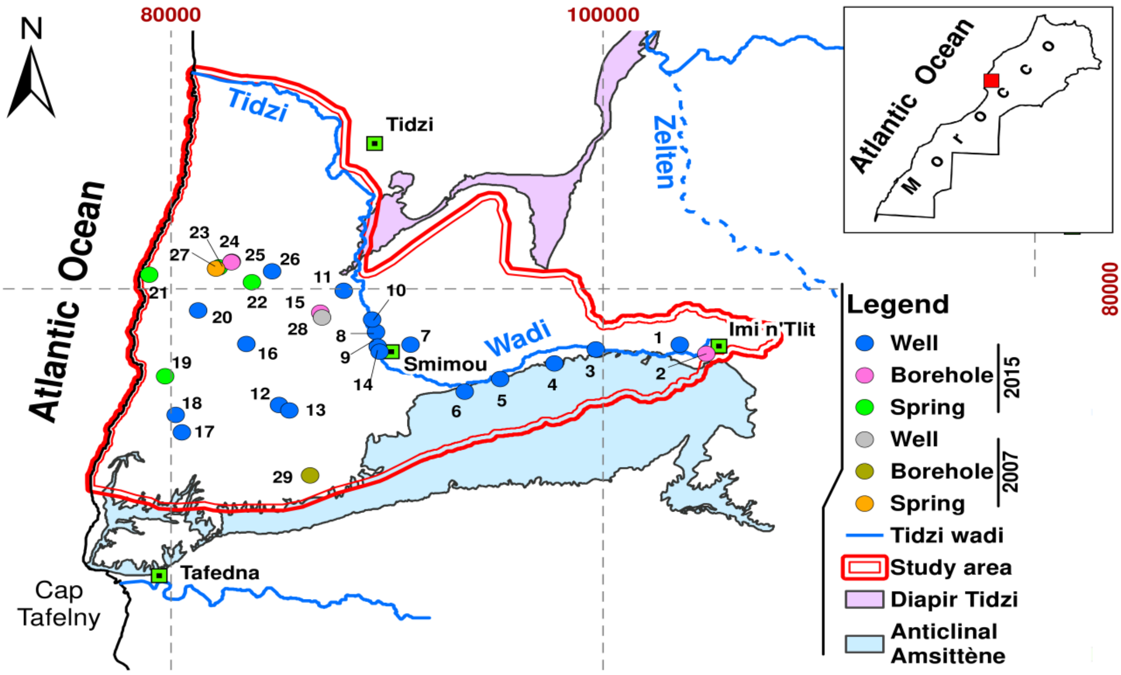


Figure 1: Geographical location of the study area and location of sampled points

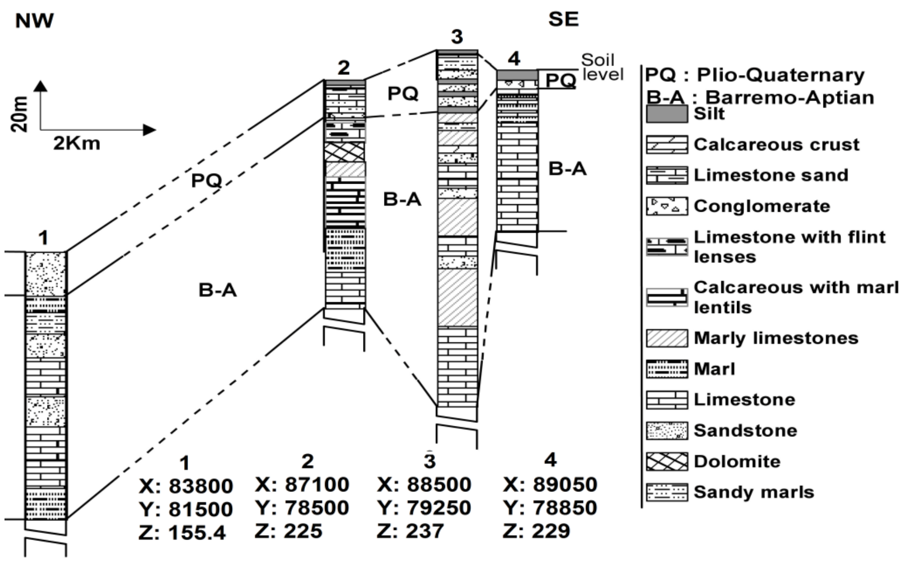


Figure 2: Lithological sections of the wells catching the Barremo-Aptian aquifer [13] (modified)

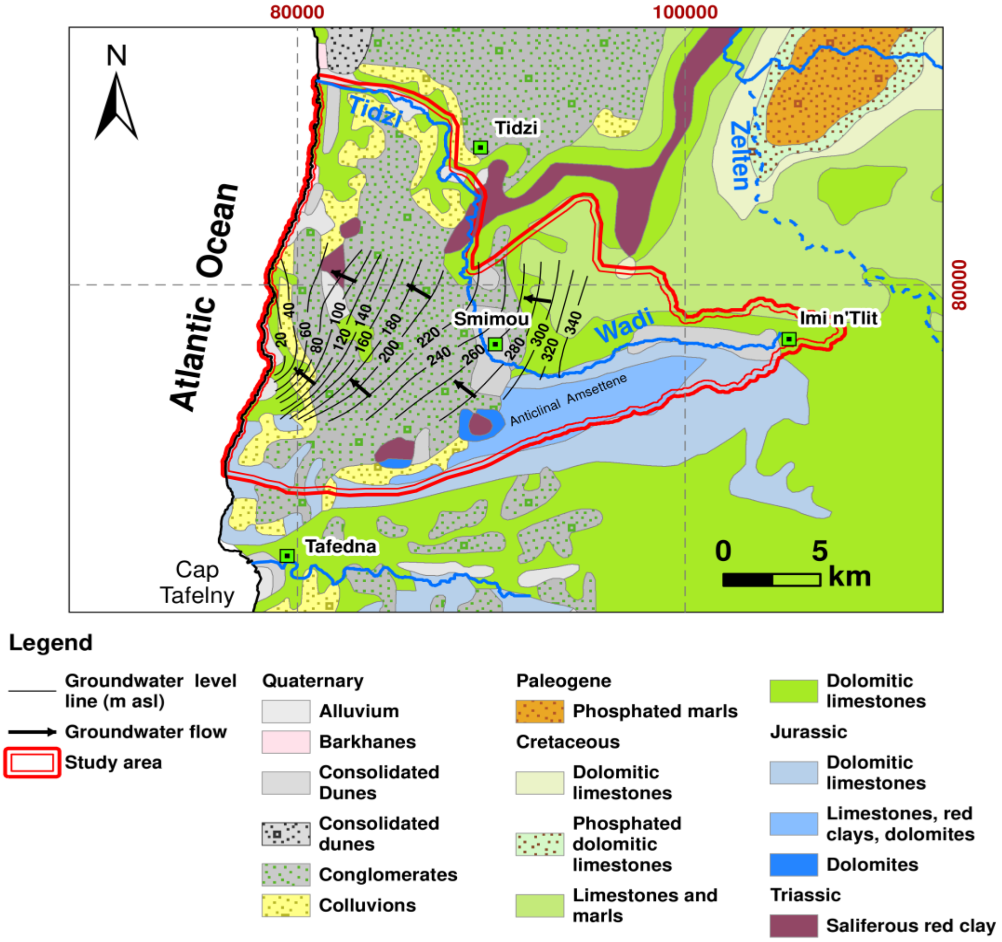


Figure 3: Geological and Piezometric map (June 2015) of the Study Area [14] (modified)

3. Material and methods

A total of 29 samples were taken from 21 wells, 5 sources and 3 boreholes collecting the Barremo-Aptian aquifer during June 2015 and October 2007. Temperature, pH and electrical conductivity (EC) were measured on the field by using a pH/mV/°C meter ADWA AD111 type and a portable conductivity meter HANNA HI-8733 type, respectively. The water level was measured by a sound probe of 200 m.

Major elements were determined by ion chromatography using DIONEX ICS-1100 in the Center for Analysis and Characterization (CAC) at the Faculty of Sciences Semlalia of Marrakech. Alkalinity was determined in situ by titration. The isotopic analyzes (Oxygen-18 and Deuterium) were carried out by mass spectrometry according to the method proposed by Friedman [15] and by Epstein and Mayeda [16]. The values are expressed in δ (‰) compared to the international standard V-SMOW (Vienna Standard Mean Ocean Water) which represents the average composition of ocean waters. The ^3H contents were measured by liquid scintillation counter following enrichment by electrolysis of the water samples [16, 17]. These contents are expressed by tritium units (TU). A Geographic Information System was used to map the spatial distribution of physico-chemical parameters.

4. Results and discussions

4.1 hydrochemistry

4.1.1 Physical parameters

Temperature

Temperature is a fundamental factor for the majority of physical, chemical and biological processes in the body of water [18]. Surface water has a temperature between 0 and 30 °C and can reach or exceed 40 °C for hot springs. As for the shallow groundwater, it usually remains constant and close to the annual mean air temperature. However, deep aquifers have higher temperatures because of the Earth's thermal gradient. The water of the Barremo-Aptian aquifer shows temperatures ranging from 18.8 °C to 25.2 °C with an average of 22.21 °C, so it is referred to as hypothermal water (<30 °C) (Figure 4). According to the simplified grid of Table 1 for assessing the overall quality of groundwater, these waters are of good quality.

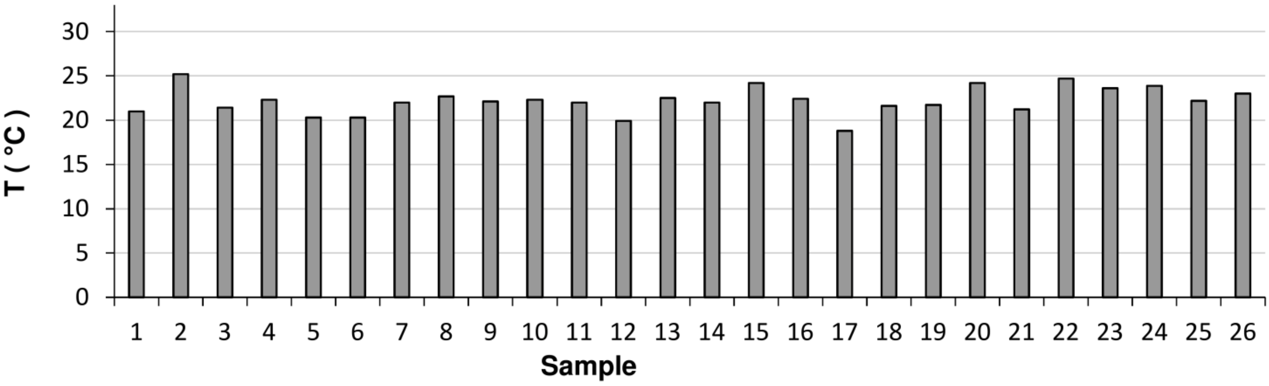


Figure 4: Variation of the groundwater temperature of the Barremo-Aptian aquifer in Essaouira basin (2015 companion)

pH

pH is a measure of the acid equilibrium of a solution and is defined as the negative of the base logarithm of the hydrogen ion concentration. It indicates the intensity of the acidic or basic character of a solution and is controlled by the dissolved chemical compounds and biochemical processes in the solution. Usually, natural waters have a pH of 6 to 8.5 [19]. Sometimes we find waters of low or high pH values, this is due to the nature of the geological formations crossed. In general, the waters circulating in limestone formations have a pH of 7.1 to 8.3 and thus constitute a vital environment favorable to the development of living organisms [20]. In our case, the water points catching the Barremo-Aptian aquifer show a pH of 7.19 to 8.18, thus meeting the standards set by the WHO (Figure 5) [21].

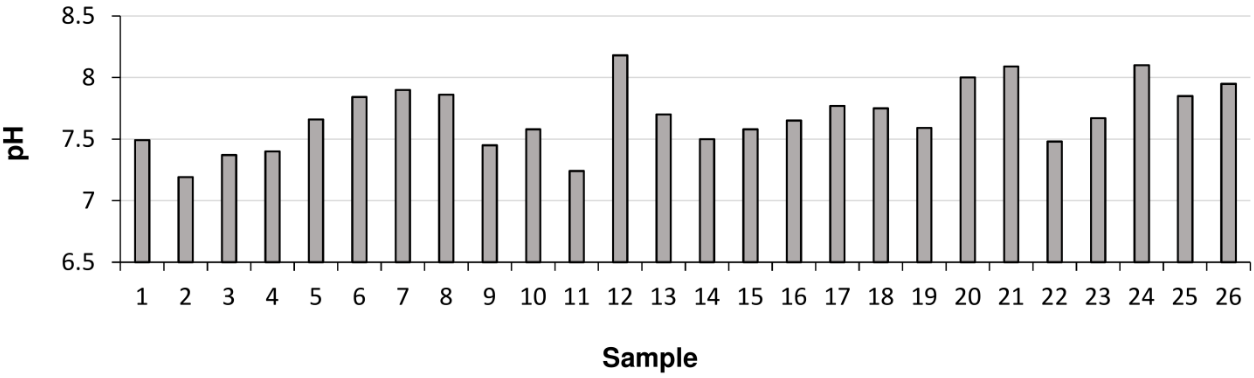


Figure 5: Variation of the groundwater pH of the Barremo-Aptian aquifer in Essaouira basin (2015 companion)

Electrical conductivity

Water electrical conductivity (EC) is the conductance of a water column between two metal electrodes (Platinum) of 1cm^2 in surface and separated from each other by 1cm, expressed in siemens per meter (s/m). It corresponds to the inverse of the electrical resistivity and is related to the concentration of total dissolved solids and major ions, which gives an indication of water mineralization degree. The EC of the Barremo-Aptian aquifer waters ranges from 490 µs/cm (sample 12) to 3650 µs/cm (sample 1) (Figure 6). Indeed, the EC distribution is irregular and is related to the nature of the geological formations where the waters lived. Based on the simplified gridof Table 1 for assessing overall groundwater quality, more than 80% of the water points sampled are of good to moderate quality.

4.1.2 Facies and chemical parameters

Chemicalfacies

Projection of major element concentrations on the piper diagram (Figure 7) indicates the dominance of the Ca-Mg-Cl type chemical facies (54%) which is located in the downstream part of the aquifer. The facies of Ca-Mg-HCO_3 type (31%) governs the upstream part. Samples 21, 24 and 25 have Na-K-Clfacies (11%) and sample 20 shows the Na-K-HCO_3 type (4%).

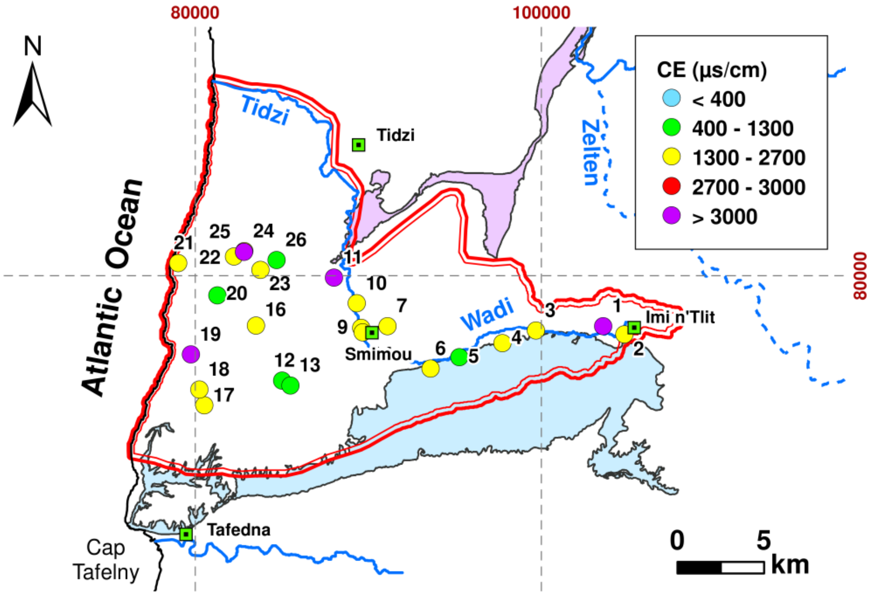


Figure 6: Spatial distribution of the groundwater electrical conductivity of the Barremo-Aptian aquifer in Essaouira basin (2015 companion)

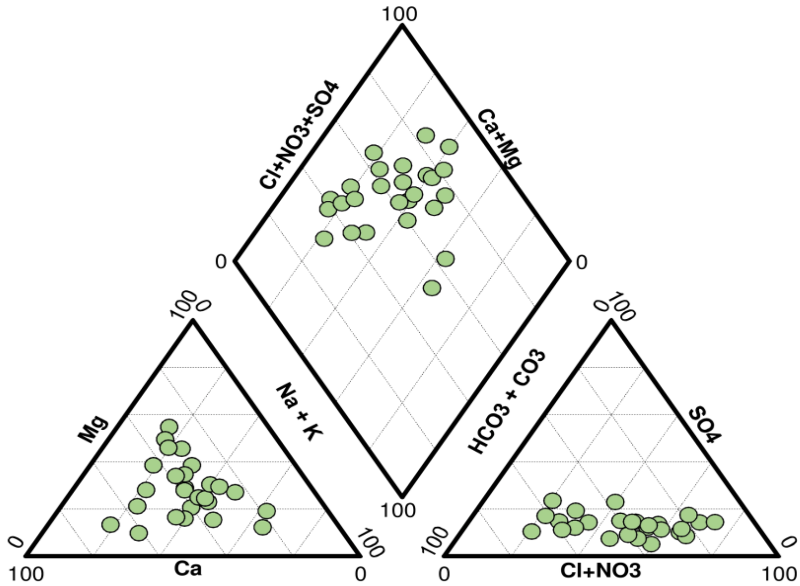


Figure 7: Piper diagram of groundwater from the Barremo-Aptian aquifer withinEssaouira basin (2015 companion)

Sodium

Sodium is a constant element of water, its concentration can range from a few tens of milligrams to 500 mg/L and even beyond. Precipitation provides only a small amount in groundwater. However, high concentrations may result from the decomposition of mineral salts (sodium and aluminum silicates), marine intrusion, infiltration of brackish water or anthropogenic activity [22, 23]. For our study area, Na levels range from 15 to 193 mg/L (Figure 8). The high concentrations are observed in the downstream part, more precisely at points 24 and 25 where the evaporite formations of the Triassic gypsifer are outcropping. However, these levels do not exceed the potability threshold set at 200 mg/L by WHO [21].

Chlorides

Chlorides are inorganic anions contained in varying concentrations in natural waters. These can acquire Cl from superficial leaching during heavy rains (arid and semi-arid zones), dissolution of evaporites, wastewater, industrial activity and from the ground, infiltration of the sea (in coastal zone) and/or brackish waters. Cl concentrations of analyzed water points (Figure 9) ranged from 34 mg/L (sample 12) to 756 mg/L (sample 19).

The high levels of Cl are marked in the downstream part where the evaporitic terrains of the Triassic gypsifer are exposed. According to Moroccan standards for the drinking water quality of groundwater, the maximum concentration in Cl recommended is 300 mg/L, while the allowable threshold is set at 750 mg/L. As a result, the waters of the Barremo-Aptian aquifer are of excellent to good quality with regard to chlorides.

Sulfates

Sulfates are found in natural waters as SO_4 ions with very different concentrations. They can come from the dissolution of gypsum, acid rain resulting from the use of hydrocarbons that emit sulfur compounds and the combustion of fossil products (coal, fuel) [22]. The waters studied have SO_4 contents ranging from 17 mg/L (sample 13) to 456 mg/L (sample 1) (Figure 10). Since the study area has no industrial activity, geological formations remain the only source of sulfates [24]. The high concentrations are observed at water point 1 and 2 (Imin'Tlit region), these concentrations resulting from the effect of the carbonate matrix and that of Cenomanian and Jurassic soils rich in gypsum. Also, samples 24 and 25 (downstream part) have high levels following the influence of Triassic saline soils. According to Table 1 and WHO standards, the waters of this aquifer remain within the standards of potability.

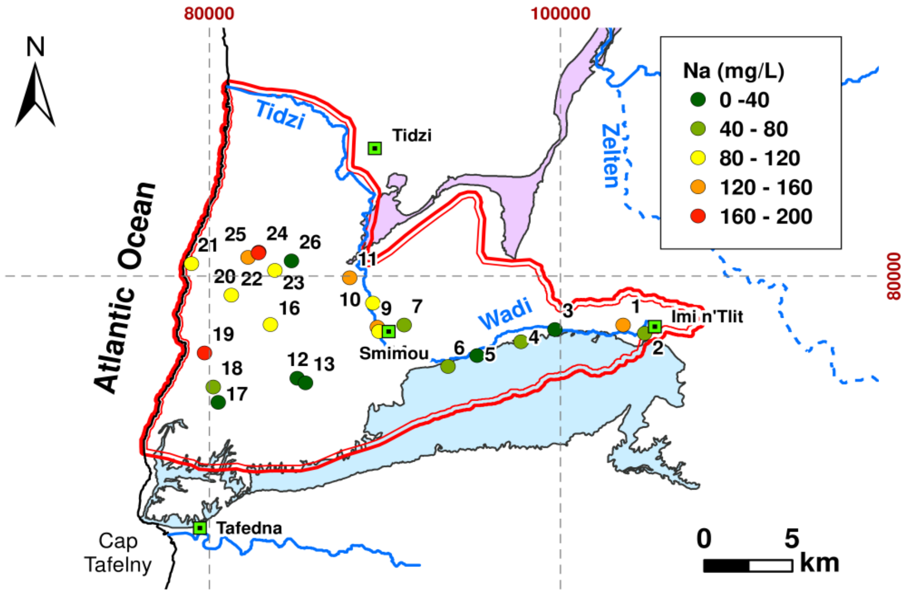


Figure 8: Spatial distribution of groundwater sodium in the Barremo-Aptian aquifer ofEssaouira basin (2015 companion)

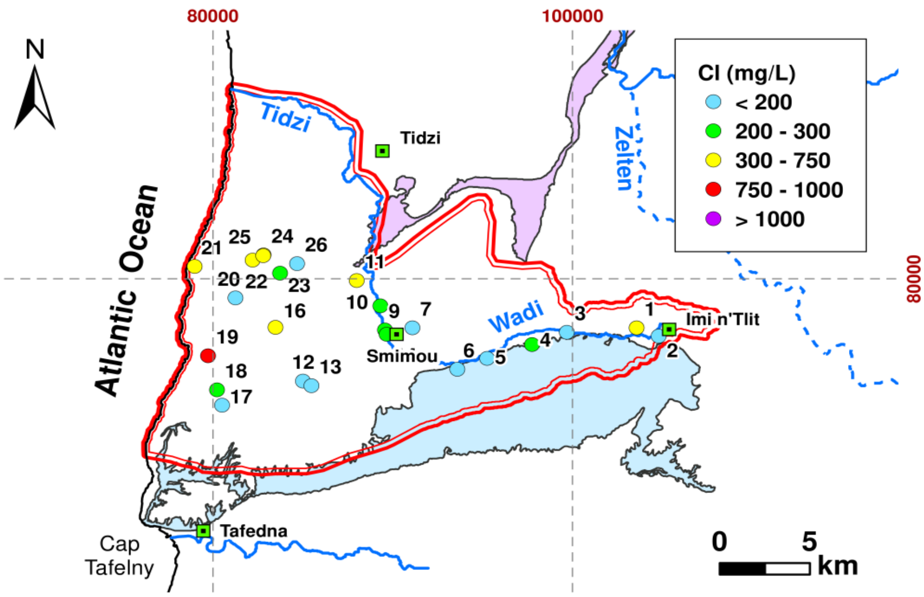


Figure 9: Spatial distribution of groundwater chlorides in the Barremo-Aptian aquifer of Essaouira basin (2015 companion)

Bicarbonates

Water alkalinity is influenced by bicarbonates (HCO_3). The content of these depends on the presence of carbonate minerals in the soil and aquifer, as well as the CO_2 content of air and soil in the catchment area [24]. Levels in unpolluted waters range from 50 to 400 mg/L [24]. HCO_3 concentrations of the analyzed points (Figure 11) range from 90 (sample 17) to 937 mg/L (sample 1). The high-grade points occupy the upstream portion of the study area where the water flows in the carbonate matrix lands.

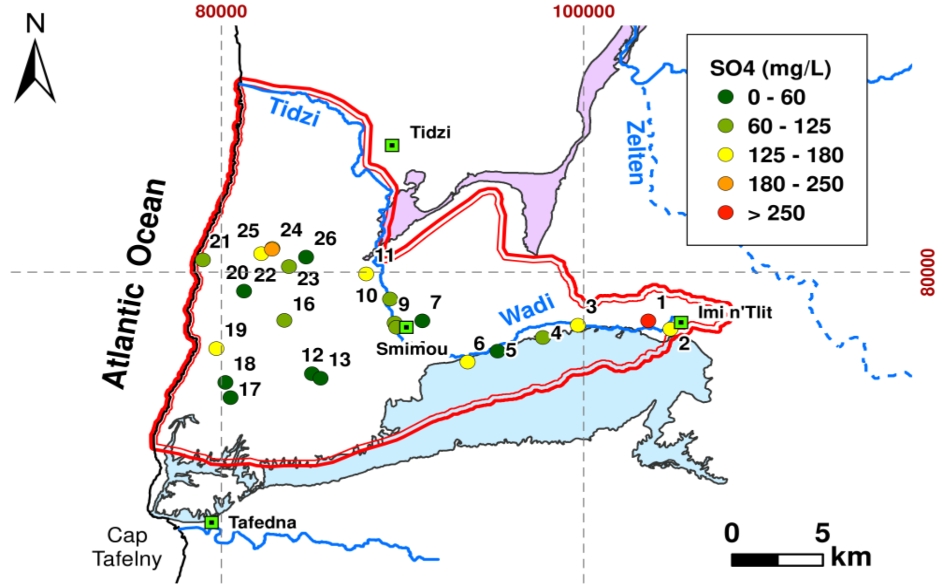


Figure 10: Spatial distribution of groundwater sulfates in the Barremo-Aptian aquifer ofEssaouira basin (2015 companion)

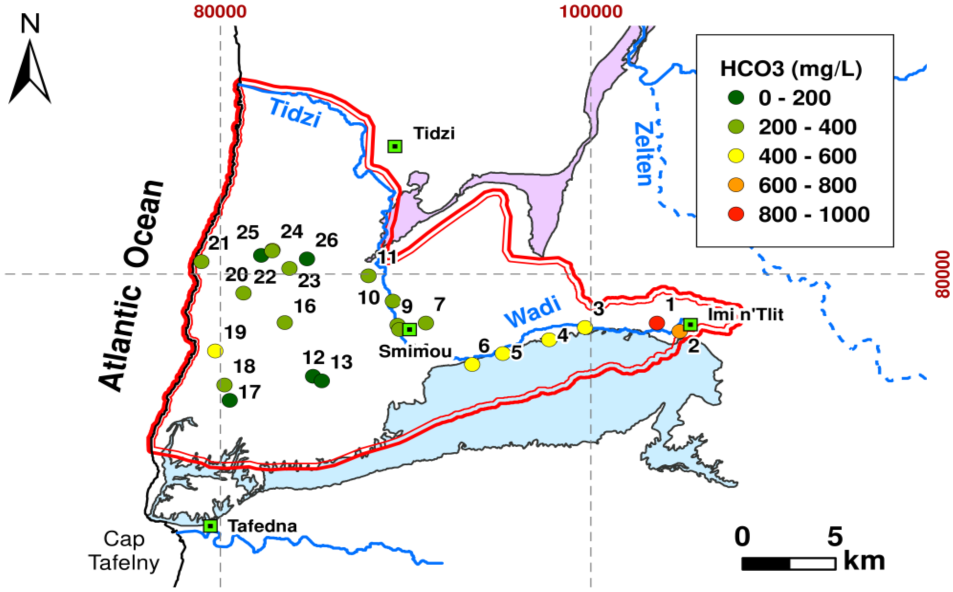


Figure 11: Spatial distribution of groundwater bicarbonates in the Barremo-Aptian aquifer of Essaouira basin (2015 companion)

Calcium

Calcium is the major component of water hardness, it is extremely common in nature and especially in calcareous rocks in the form of carbonates. Its content varies mainly according to the nature of the formations crossed. The points taken from the Barremo-Aptian aquifer show Ca contents ranging from 37 to 223 mg/L (Figure 12). Except for the samples 1, 4 and 11, the rest show concentrations in the range 31 to 160 mg/L which corresponds to the standards of potability. High levels of Cabe attributed to the dissolution of calcite and/or dolomite as well as other calcium minerals such as gypsum.

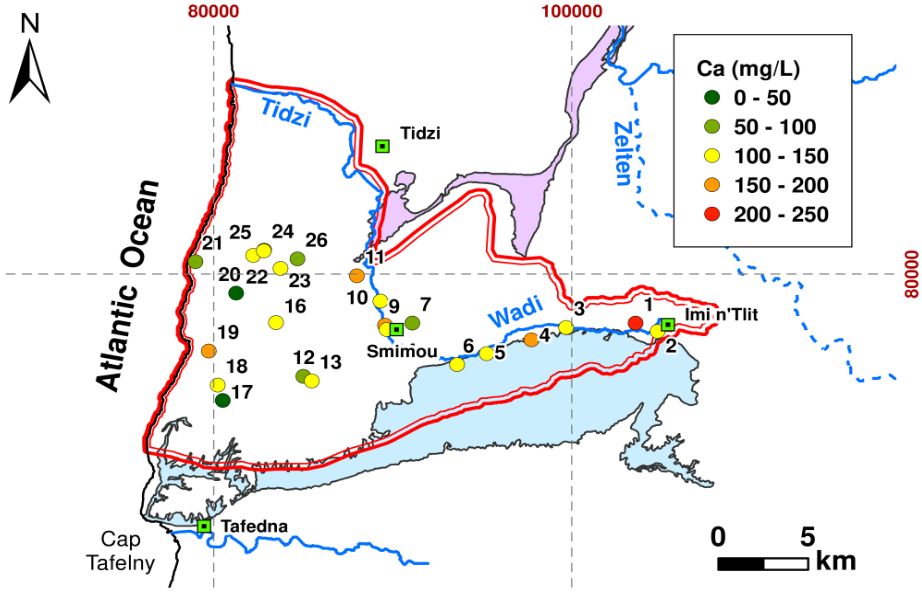


Figure 12: Spatial distribution of groundwater calcium in the Barremo-Aptian aquifer ofEssaouira basin (2015 companion)

Magnesium

Magnesium is one of the most common elements in nature. Its geological abundance and wide industrial use mean that levels in the water can be significant. This significant element of water hardness can come from dolomitic and dolomite limestones of the Jurassic or Middle Triassic. The analyzed samples (Figure 13) show Mg contents ranging from 6 to 200 mg/L. Excluding items 1, 2, 3 and 11, all the samples record concentrations below 100 mg/L, the maximum limit of the Moroccan standard for potability. High levels in the upstream portion of the study area are due to the effect of Cenomanian dolomitic limestones and Jurassic dolomites of the Amsittene anticline. But those observed at sample 11 reflect the influence of Triassic saline soils.

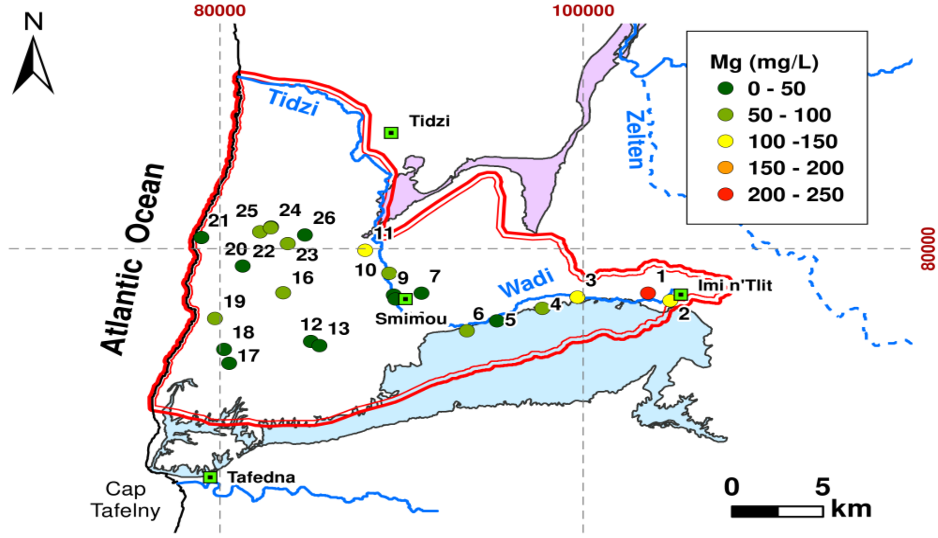


Figure 13: Spatial distribution of groundwater magnesium in the Barremo-Aptian aquifer of Essaouira basin (2015 companion)

Potassium

Potassium is generally the least abundant element in water after Na, Ca and Mg. It contributes very little to the mineralization of natural waters with an almost constant presence that does not usually exceed 10 to 15 mg/L. Potassium is found in the form of double chlorides in many minerals such as corrollite and sylvinite. It is also found in the ashes of plants in the form of carbonate. Potassium is an essential element for life and especially for the growth of plants. In the field of agriculture, it is used as fertilizer in the form of potassium sulfate, potassium chloride or potassium nitrate. The Barremo-Aptian aquifer has K contents ranging from a low of 11.30 mg/L (sample 26) to a high of 111.06 mg/L (sample 14) (Figure 14). According to these grades in K, all the water points sampled, excluding 13 and 26, do not meet the potability standards announced by the WHO in 2011 [21].

Figure 13: Spatial distribution of groundwater nitrates in the Barremo-Aptian aquifer of Essaouira basin (2015 companion)

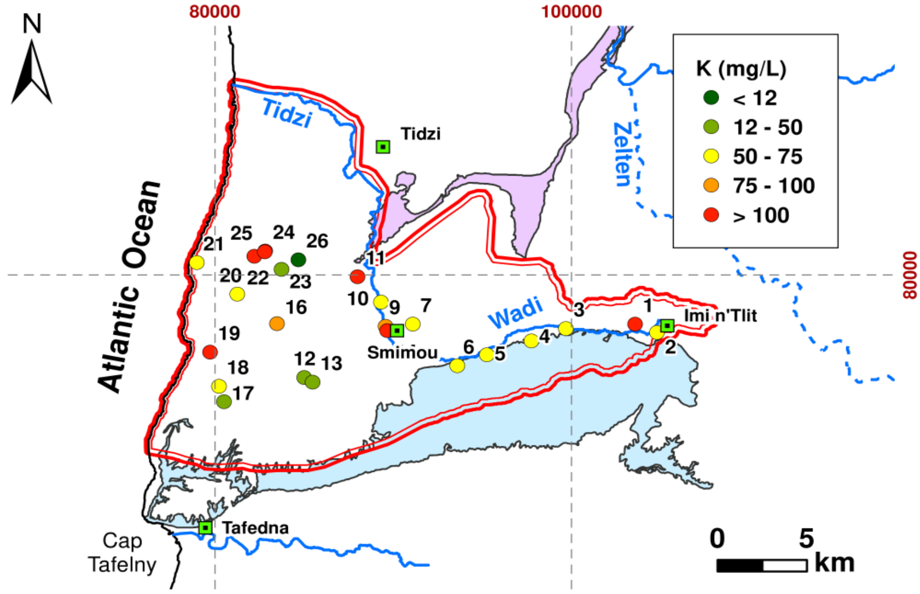
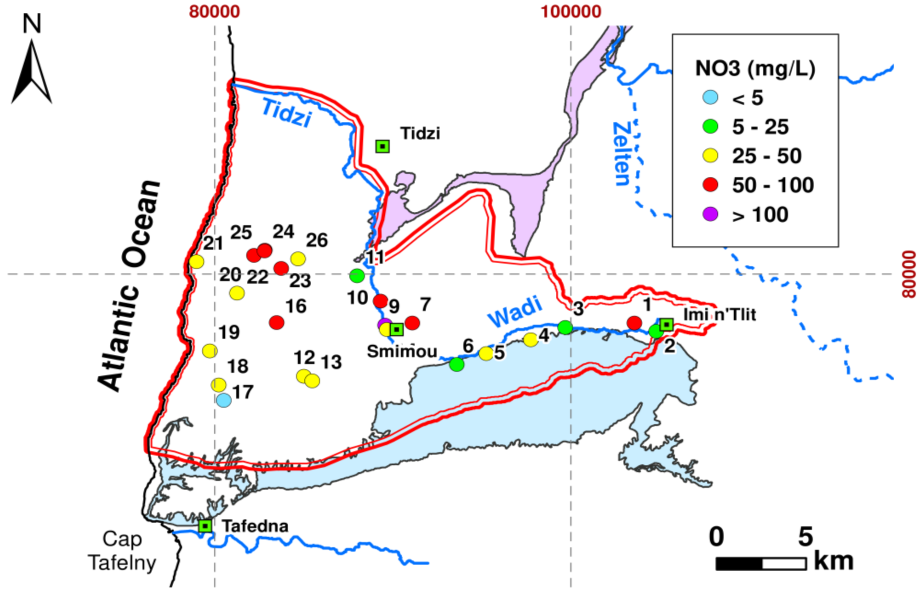


Figure 14: Spatial distribution of groundwater potassium in the Barremo-Aptian aquifer of Essaouira basin (2015 companion)

Nitrates

Nitrates are present in water by the leaching of nitrogen products into the soil by decomposition of organic matter or synthetic or natural fertilizers [26]. In unpolluted natural waters, the nitrate level is very variable (from 1 to 15 mg/L) depending on the season and the otrigin. The high NO_3 content of ground and surface water is often linked to livestock development, excessive fertilization of agricultural areas by fertilizers, manure and slurry and domestic pollutants. NO_3 levels in the study area range from 2.60 to 155.70 mg/L (Figure 15). Of all the water points sampled, 8 water points showed levels of NO_3 higher than the norm accepted by WHO and Morocco (50 mg/L).



Due to the food nature of the agriculture practiced in the study area, intake by plants and fertilizers is negligible or non-existent. However, high levels of NO_3 would come from domestic pollutants, as this pollution is a one-off phenomenon. Only the catchment points are polluted and this pollution originates from the traditional methods of drawing. These result in a significant amount of water flowing around the catchment wells, constituting quasi-permanent pools that are enriched in NO_3 by livestock waste during watering. The highest concentration recorded at water point 9 would be caused by the Smimoucenter's landfill.

Planning, Housing and the Moroccan Environment, 2010)

4.1.3 Overall water quality of the Barremo-Aptian aquifer

The assessment of water quality of the Barremo-Aptian aquifer from Essaouira coastal zone basin was followed by the three elements listed in Table 2. This gives the electrical conductivity, the Cl and NO_3 samples collected in June 2015. Based on the simplified grid of groundwater of Table 1, determined by the Minister of Equipment and the Minister of Planning, Urban Planning, Habitat and the Environment, 50% of Barremo-Aptian aquifer waters have a medium quality, 27% show poor quality and the rest have very poor quality (Figure 16).

Poor and very poor quality would generally result from the presence of nitrates with contents which exceed widely the standards of potability fixed at 50 mg/L, it is the case of the water points 1, 7, 8, 9, 10, 15, 16, 22, 23, 24 and 25. Since the agriculture practiced in the study area is of a foodstuff nature, these NO_3 levels could only come from domestic pollution. That is to say that this pollution is punctual and occurs around the wells where a significant portion of water is discharged, forming quasi-permanent ponds rich in NO_3 following livestock waste during watering. The effect of the reservoir rock in which the water was staying could also be felt as is the case for samples 1, 11, 19 and 26.

	Parameter		
Quality	EC (µs/cm)	Cl (mg/L)	NO_3 (mg/L)
Very good	< 400	< 200	< 5
Good	400-1300	200-300	5-25
Medium	1300-2700	300-750	25-50
Poor	2700-3000	750-1000	50-100
Verypoor	> 3000	> 1000	> 100

	Parameter			
Sample	EC (µs/cm)	Cl (mg/L)	NO_3 (mg/L)	Global quality
1	3650	579.90	71.49	Très mauvaise
2	1640	175.67	9.18	Moyenne
3	1700	121.40	11.75	Moyenne
4	1776	204.34	42.10	Moyenne
5	1280	76.17	42.94	Moyenne
6	1530	106.50	5.27	Moyenne
7	1351	110.83	84.17	Mauvaise
8	1365	165.30	100.25	Très mauvaise
9	2330	266.23	155.72	Très mauvaise
10	1750	250.16	64.60	Mauvaise
11	3250	635.30	20.33	Très mauvaise
12	490	34.10	35.00	Moyenne
13	966	149.05	37.39	Moyenne
14	2040	241.98	39.21	Moyenne
15	1799	274.09	78.77	Mauvaise
16	2120	356.50	81.44	Mauvaise
17	2090	88.40	2.59	Moyenne
18	1430	214.77	43.68	Moyenne
19	3580	755.77	35.61	Très mauvaise
20	1291	142.76	30.29	Moyenne
21	1875	336.18	34.99	Moyenne
22	2640	514.77	68.52	Mauvaise
23	1820	263.28	69.45	Mauvaise
24	2400	320.80	58.11	Mauvaise
25	3400	637.35	70.44	Très mauvaise
26	624	41.23	47.74	Moyenne

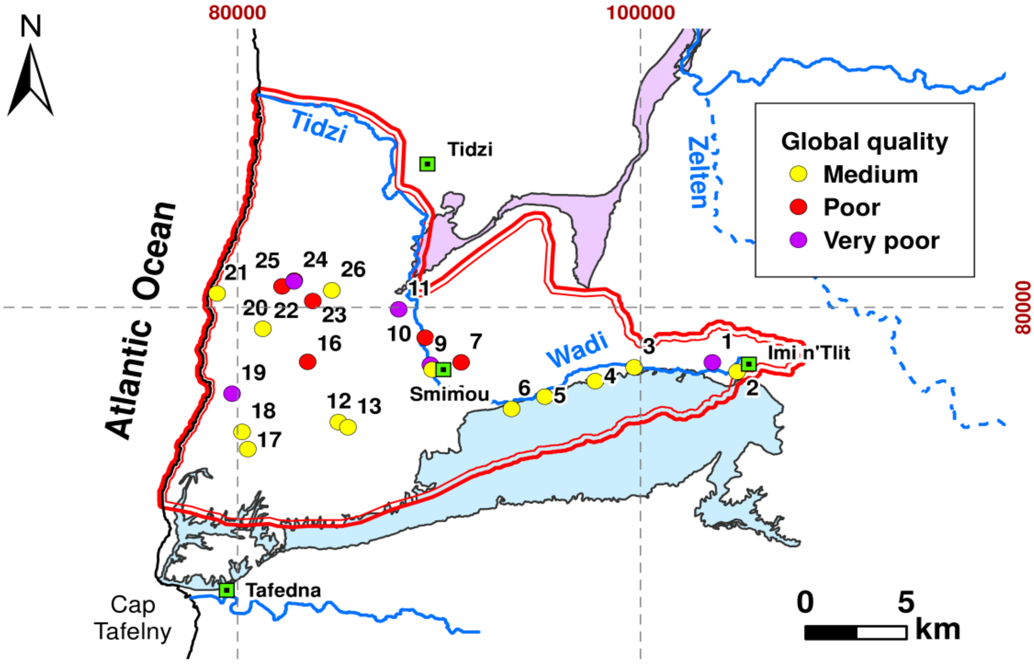
Figure 16: Global groundwater quality of the Barremo-Aptian aquifer within Essaouira basin

4.2 Stable isotopes

The use of stable isotopes of the water molecule, especially 18-Oxygen, has become a necessary tool for the study of groundwater [26-28]. This technique makes it possible to (i) determine the origin and history of the water, (ii) estimate the areas and recharge conditions of the aquifers and (iii) determine their relationship with each other and with surface water (rainfall,runoff).

For the Barremo-Aptian aquifer, the number of water points analyzed for oxygen-18 is very small but provides a first approach to groundwater ^{18}O contents and an estimate of their recharge altitude. Table 3 summarizes the results of the groundwater ^{18}O and ^{2}H measurements of the Barremo-Aptian aquifer.

The stable isotope composition of samples collected in October 2007 is given in Table 3 and ranged from -4.59 to -4.49 ‰ and from -25.61 to -22.26 ‰ for ^{18}O and ^{2}H respectively. The representation of these contents on the



correlationdiagram^{18}O-^{2}H (Figure 17) shows that all the points are located above the Global Meteoric Water Line (GMWL) [29] and near the Local Meteoric Water Line (LMWL), determined by [30]. This reflects a fast recharge without evaporation by precipitation of oceanic origin. The ^{18}O levels are almost the same for all the points, which allows us to say that the Barremo-Aptian aquifer has only one group of water. According to the ^{18}O regional gradient equation according to the altitude (1) established by [31] in Atlas of Bni-Mellaland confirmed by Bahir in 2004, the recharge altitude of the Aghbalou source located at an altitude of 100 m asl is about 611 m asl. As for the borehole of IddaOuAzza, which is at an altitude of 382 m asl, its recharge is carried out at an altitude of 573 m asl, passing through the Tigoudine well, whose altitude is 255 m asl and the recharge area is about 588 masl (Figure 18).

$\delta^{18}O = (-2.6\ 10^{-3}\ x\ Altitude)-3$ (1)

However, the recharge altitude of the Barremo-Aptian aquifer is estimated at 600 masl on the outcrops of the Barremian-Aptian formations in the East.

Tritium (^{3}H) is the radioactive isotope of hydrogen. It is characterized by a half-life of 12.43 years, hence its importance in the study of relatively short hydrogeological cycles [32]. In general, water with contents of ^{3}H <1TU is considered to have a pre-1952 age, the date of the beginning of nuclear tests [33]. However, ^{3}H concentrations above 1TU indicate recent water infiltration. Table 3 groups the samples that have measured ^{3}H. These have contents ranging from 0.8 to 1.2 TU, which reflects that the recharge of the Barremo-Aptian aquifer is pre-nuclear, i.e. before the time of the thermonuclear bomb test. As a result, the presence of old waters indicates a low turnover rate. This must be absolutely taken into account in the operation and management of this aquifer. Its exploitation by uncontrolled pumping can lead to hydrochemical equilibrium and consequently an irreversible degradation of the quality of the water as well as a depletion of the resource.

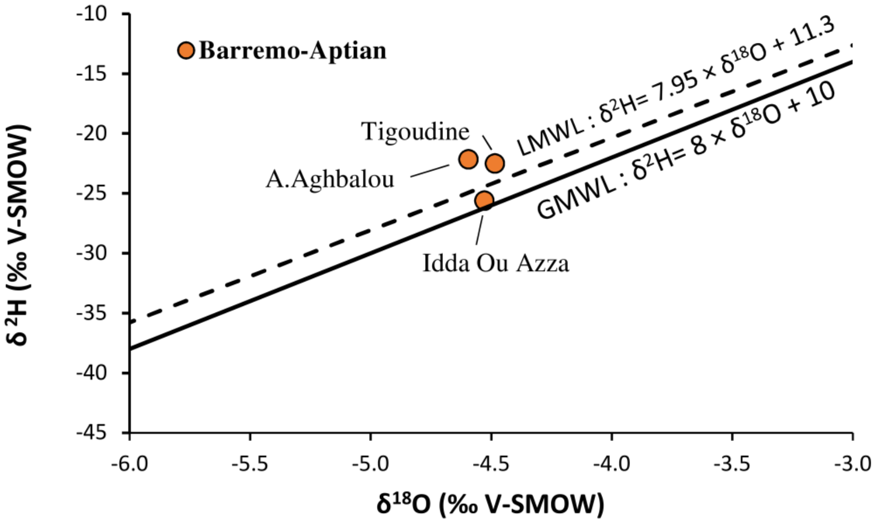


Figure 17: ^{2}H-^{18}O correlation diagram of the groundwater of the Barremo-Aptian aquifer fromEssaouira basin

Table 3: Results of isotopic analyzes of sampled water points (October 2007)

Sample	X (Km)	Y (Km)	Emergence altitude (masl)	Estimation de l'altitude de recharge (masl)	δ^{18}O (‰ VSMOW)	δ^{2}H (‰ VSMOW)	^{3}H (TU)
Aghbalou	82.10	81.05	100	611	-4.59	-22.15	1
Tigoudine	87.00	78.50	255	588	-4.53	-25.61	1.2
Idda ou Azza	86.45	70.30	382	573	-4.48	-22.49	0.8

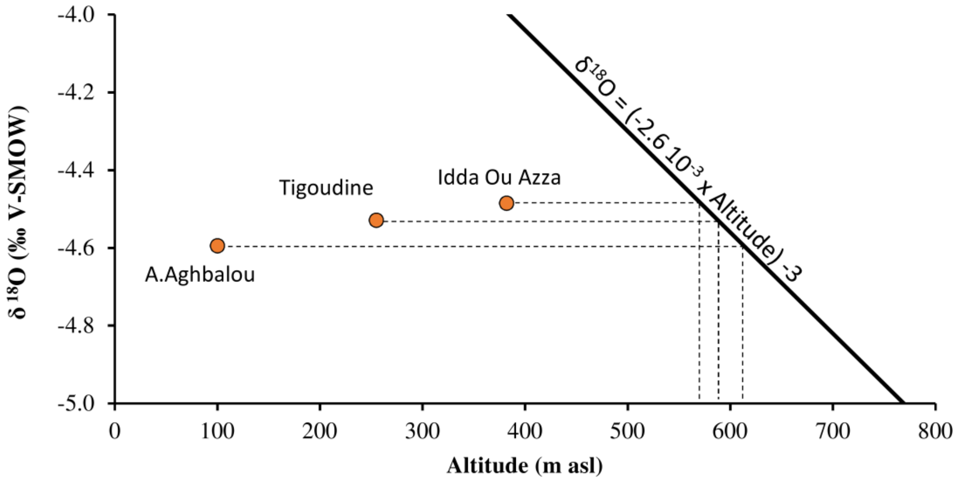


Figure 18: Determination of the average recharge altitudes of the Barremo-Aptian aquifer in Essaouira basin using Oxygen-18 contents

Conclusion

The objective of this study was to evaluate the water quality of the Barremo-Aptian aquifer from the Essaouira basin.

The hydrochemical approach made it possible to define the chemical facies of the water, to estimate the origin of the chemical elements and to specify their quality. The upstream part of the Barremo-Aptian aquifer shows a Ca-Mg-HCO_3 type facies, while that of the downstream part is of the Ca-Mg-Cl type.

In terms of water quality, 50% of the water points of the Barremo-Aptian aquifer have a medium quality, the rest show a poor to very poor quality. The deterioration in quality would be mainly due to the presence of nitrates, which seem to be linked to quasi-permanent puddles, rich in NO_3 following livestock waste, which take place around wells during watering.

The isotopic study shows that the Barremo-Aptian aquifer recharge is ensured by direct infiltration, without evaporation, of precipitations of oceanic origin and that this recharge is carried out at an altitude of 600 m asl, in the East of the study area, where the formations of Barremian and Aptian are exposed. This aquifer has ancient waters indicating a low rate of renewal.

However, the study area has yielded certainly interesting results, which must be taken into account for a better management and protection of this resource, with a low rate of renewal, thus raising the awareness of the populations of the region: (i) to avoid contamination groundwater by NO_3 from livestock waste during watering, (ii) adopt a rational exploitation strategy and (iii) make them aware of the low renewal rate of this aquifer and its vulnerability to climate conditions.

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