Quantitative and Qualitative Assessment of Groundwater from Semi-Arid Zones in the Context of Climate Change, Example of Essaouira Region, Morocco

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Abstract

This study aims to assess the effect of climate change on water resources in semi-arid environments, taking the Essaouira region as an example. Analysis of climate data shows a downward trend in precipitation of 12 to 16% and an increase in air temperature of 2.3 °C over the past three decades. The piezometric study shows a continuous drop in the piezometric level which exceeds 12 m for the Cenomanian-Turonian aquifer, 17 m for the Plio-Quaternary aquifer, around 8 m for the Barremian-Aptian aquifer and 5 m for the Hauterivian. Hydrogeochemical analysis shows that (i) the groundwater mineralization is controlled by the dissolution of evaporitic and carbonates minerals, by the reverse ions exchange phenomenon, and by the marine intrusion, especially at Plio-Quaternary aquifer; (ii) the groundwater quality in the study area deteriorates gradually over time and space. The isotopic technique shows that (i) the groundwater recharge in the study area is ensured by precipitation of oceanic origin without significant evaporation and that (ii) climate change has no remarkable effect on the isotopic content of the groundwater of the study area. However, the results of this article reflect that the Essaouira basin is very vulnerable to climate change.

Introduction

Climate change is a global problem, involving the long term complex interactions between environmental factors and economic, social, technological and political conditions which cause significant effects at regional level (Lebel and Vischel 2005; Alpert et al. 2008; Misra 2014), including the Maghreb region (Bahir et al. 2016; El Kharraz 2012; Ouhamdouch et al. 2018, 2020; Ragab and Prudhomme 2002).

In arid and semi-arid regions, rainfall is one of the determining factors of climatic characterization. The study of recent evolution in climate is an essential tool to determine optimal general solutions to the problems resulting from the relationship between water requirement and their availability, and therefore better management of water resource (Bahir et al. 2018, 2019; Carreira et al. 2018; Ragab and Prudhomme 2002).

Studies on climate change show that global warming in the Maghreb country is significant than the global average. Indeed, on a global scale, the increase estimated at 0.74 ° C in the 20th century, while it was oscillated between 1 and 2 ° C on the Mediterranean scale and the region of North Africa (GIEC 2007; Green et al. 2011; Ouhamdouch et al. 2018, Ragab and Prudhomme 2002). As for precipitation, it has decreased in the Mediterranean region, in the Sahel, in southern Africa and in certain parts of South Asia at different temporal and spatial scales (Alpert et al. 2008; IPCC 2013).

Morocco, like the Mediterranean countries (Vicente-Serrano 2006), have suffered from several periods of drought (Bahir et al. 2002; Driouech 2010; Babqiqi 2014). Its water resources are limited; they are estimated at 20 billion cubic meters, or an average of 700 m³/year/inhabitant, which corresponds to a situation of fairly high water stress. The number of years in rainfall deficit is greater than the number of wet years (Driouech 2010; Stour and Agoumi 2009; Sinan et al. 2009), especially the cycles of 1980–
1985, 1990–1995 and 2007–2010. According to Babqiqi (2014), the comparison of the average annual temperatures over the two periods 1971–1980 and 1998–2007 shows an increasing trend (from 0.3 to 2.5 °C depending on the region).

This decrease in precipitation and the increase in temperatures linked to the climate change are likely to have a negative impact on water resources, especially in arid and semi-arid areas.

In these regions, few studies have been done to assess the climate change impact on water resources, but they are generally focused on surface water (Abutaleb et al. 2018; Hallouz et al. 2019; Xu et al. 2004). Some other studies have evaluated the global warming effect on groundwater by limiting ourselves to the piezometric and/or hydrochemical approach (Al-Maktoumi et al. 2018; Berhail 2019; Lachaal et al. 2018). For this study to be original, we assessed the impact of climate change on the water resource of the Essaouira basin (Morocco) by combining several approaches such as hydroclimatology, piezometry, hydrochemistry and isotopy.

**Study area**

The study area, called the Essaouira syncline basin, covers an area of 6000 km². It is part of the Atlantic Atlas, which is the westernmost part of the southwestern Moroccan basin (Dresh 1962; Duffaud 1960). This basin is bounded to the north by Hadid anticline, to the south by Tidzi wadi, to the east by the Bouabout region, and to the west by the Atlantic Ocean. It is subdivided into two parts, the first known as the “Bouabout unit” (upstream part) and the second known as the “coastal zone” (downstream part) (Fig.1).

From a morphological point of view, the study area is made up of a set of synclinal basins filled with formations ranging from the Triassic to the Quaternary (Fig.2). The elevations vary between 400 and 1600 m for the upstream part and less than 400 m for the downstream part. Hydrographically, the study area is characterized by a less-developed network. This is mainly represented by Ouazzi wadi in the North and Igouzoullene wadi in the South, passing through Ksob wadi resulting from the confluence of Igrounzar and Zelten wadi and through Tidzi wadi. All of these wadis flow into the Atlantic Ocean (Fig.2).

Geologically and hydrogeologically, the upstream part of the study area is marked by the outcrop of formations of Middle and Upper Cretaceous age, in particular, Albian-Vraconian, Cenomanian and Turonian (Duffaud 1960; Amghar 1989) (Fig.3). These formations are composed of limestone and dolomitic benches interspersed with marl and sandstone. The Albian-Vraconian formations contain sandstone and limestone dolomites alternating with sandstone banks and sandy clays.

The Cenomanian (about 200 m thickness) is represented by alternating marls with anhydrite, lumachellic and dolomitic limestones. As for the Turonian, it is composed of limestones with an abundance of silica. These synclines contain important water reservoirs, notably the Cenomanian-Turonian aquifer which
remains the most important in the region. According to Jalal et al. (2001), this aquifer has transmissivities varying between $2.2 \times 10^{-4}$ and $2.7 \times 10^{-1}$ m²/s.

The downstream part contains 2 important aquifers: (i) the Plio-quaternary and the (ii) Turonian in the northern part, between Ksob wadi and Tidzi wadi, (iii) the Barremian-Aptian located between Tidzi wadi and Amssittene anticline and (iv) the Hauterivian, southern limit of the study area, is interposed between the Amssittene anticline and Igouzoullene wadi (Fig.2).

The Plio-quaternary is characterized by a matrix of limestone sandstone. It contains an important water table, the wall of which is formed in the synclinal structure by the marls of Senonian (Fig.3).

According to Mennani (2001), this water table has transmissivities varying between $6.1 \times 10^{-2}$ and $4.5 \times 10^{-5}$ m²/s.

As for the Turonian, represented by limestones, it contains a captive aquifer under the Senonian marls in the synclinal structure and probably in direct contact with the Plio-Quaternary at the confines of this structure (Fig.3). It has a transmissivity ranging between $0.8 \times 10^{-4}$ and $2.7 \times 10^{-2}$ m²/s (Mennani 2001).

The Barremo-Aptian aquifer contains Barremian formations (about 70 m thickness) represented by an alternation of gray marl (with traces of gypsum), fractured fossiliferous limestones and sandstone and Aptian formations (about 100 m thickness) composed of red clays and sandstone with intercalations of dolomitic sandstones or bioclastic limestones (Duffaud 1960; Duffaud et al. 1966) (Fig.3). The transmissivity is of the order of $1.5 \times 10^{-3}$ m²/s (Mennani 2001).

The Hauterivian aquifer, whose thickness is about 200 m, is composed of marly clays and fractured siliceous limestones, marly and dolomitic limestones more or less fractured (Fig.3) (Duffaud 1960; Duffaud et al. 1966). According to Mennani (2001), this aquifer has transmissivities varying between $1.6 \times 10^{-5}$ and $6.7 \times 10^{-5}$ m²/s.

**Materials And Methods**

In this investigation, the results of nine campaigns 1990, 1995, 1997, 2009, 2015, 2016, 2017, 2018 and 2019 were used to assess the quality of groundwater in the Essaouira region in the context of climate change. Electrical conductivities, temperatures, pH and nitrates were measured in situ with a portable conductivity meter (HI9829 multiparametric instrument), and the depth of the water level was measured using a 200 m piezometric probe.

The analyses of the chemical elements were carried out at the Laboratory of Hydrogeology at the Faculty of Sciences Semlalia of Marrakech (Morocco) for the campaigns 1990 to 2009. As for that of 2015 to 2019, the analyses were carried out at the Laboratory of Geosciences and Environment- ENS at the Ecole Normale Superieure of Marrakech (Morocco). The $\text{SO}_4^{2-}$ anion contents were determined by the nephelometric method (Rodier et al. 2009). Concentrations of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ cations were measured by
the complexometry method (EDTA) and those of Cl by the Mohr method (Rodier et al. 2009). The Na+ and K+ contents were determined by flame photometry (Rodier et al. 2009). As for HCO₃⁻ contents, they were determined by titration using a sulfuric acid solution. All the samples display an ion balance of less than 10%, which allowed us to validate the obtained results. The obtained results are grouped in Appendix 1.

A total of 46 points collected, in April 2016 (22 points) and in May 2018 (24 points) were analyzed for stable isotopes (oxygen–18 and deuterium) and radioactive (Tritium). The 22 samples taken in 2016 represent the Cenomanian-Turonian aquifer (the upstream part of the study area) and 24 water points taken in 2018 represent the Plio-Quaternary aquifer (18 samples), 4 the Turonian aquifer (4 samples) and surface water (2 samples).

The analysis of stable isotopic elements (δ²H and δ¹⁸O) were carried out at the Nuclear Technology Institute in Lisbon (Portugal) and the Laboratory of Radio-Analysis and Environment (LRAE) at the National School of Engineers of Sfax (Tunisia) by applying the mass spectrometry method (Friedman et al. 1953; Epstein and Mayeda 1953). The tritium (³H) content was determined by the technique of electrolytic enrichment followed by the liquid scintillation counting method (Lucas and Unterweger 2000) at Nuclear Technology Institute in Lisbon (Portugal).

A Geographic Information System (GIS) was used to map the spatial distribution maps of the electrical conductivity and the physicochemical elements.

The PHREEQC program (Parkhurst and Appelo 1999) was used to calculate the saturation indices (SI) using the following formula: SI = log (KIAPKSP)

With: KIAP is the product of the ionic activity of ions. KSP is the mineral solubility product. The saturation index corresponds to the deviation from the equilibrium of the water from the mineral phase. If SI = 0, the water is in equilibrium; SI is negative, the water is undersaturated with respect to the mineral; SI is positive, the water is supersaturated with respect to this mineral.

**Results And Discussion**

**Climatic parameters (Precipitations and temperatures)**

The climate parameter data used in this study were obtained from the Tensift Hydraulic Basin Agency (ABHT).

Analysis of precipitation data for an observation period of 38 years (1978–2015) for the study area reveals significant variability on an annual scale (Fig.4).

Indeed, this rainfall is subject to fluctuations from one year to another, with wet and other dry periods of two to five consecutive years. The height of the precipitated sheet of water varies between a minimum of 135 mm, measured in 2008 and a maximum of 707 mm measured in 1996 with an average of 304 mm.
The application of the Pettitt test (Pettitt 1979) (Table 1), with a 90% confidence level shows the presence of a break in the pluviometric series in 1999. This test made it possible to split the rainfall series into two sub-series. The average of annual rainfall before and after this break is $A_1 = 313.8$ (first sub-series) and $A_2 = 263.4$ (second sub-series) mm, respectively. This makes it possible to estimate a rainfall deficit of 16%. The results of the Mann-Kendall trend test (Table 1) displays a negative multivariable standard normal ($U_{MK}$) ($U_{MK} = -1.09$). This reflects a downward trend in precipitation and confirms the results of the Pettitt test.

### Table 1. Statistical tests

| Test          | Formula                                                                 | Reference   |
|---------------|-------------------------------------------------------------------------|-------------|
| Pettitt       | $U_T = \sum_{t=1}^{T} \sum_{i=1}^{T} D_{ij}$                          | Pettitt 1979|
|               | $\text{With: } D_{ij} = -1 \text{ si } (x_i-x_{i+1})>0, D_{ij} = 0 \text{ si } (x_i-x_{i+1})=0, D_{ij} = 1 \text{ si } (x_i-x_{i+1})<0.$ |             |
| Mann-Kendall  | $U_{MK} = \frac{S}{\sqrt{\text{Var}(S)}}$                             | Mann 1945, Kendall 1975 |
|               | $\text{With: } S = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \text{sgn}(a_j - a_i)$ and $V_{MK}(s) = \frac{\text{min}(1,2n-5)}{18}$ |             |
|               | The trend is upward if $U_{MK}>0$, downward if $U_{MK}<0$               |             |

The evolution study of annual atmospheric temperatures was carried out over for 28 years (1987–2015). Maximum temperatures range between 29.3 and 37.2 °C with an average of 34.2 °C. As for the minimum temperatures, they range between 2.4 and 9.3 °C with an average of 7.4 °C. While the average temperatures, vary between 17.7 and 22.4 °C with an average of 20 °C (Fig.5a).

The application of the Pettitt test with a significance level equal to 5% shows the existence of a significant break in the series of maximum, average and minimum annual temperatures, respectively in 1999, 2000 and 1994 (Fig.5b). For the maximum annual temperatures, the average before and after this break is 32.75 and 35.53 °C, with an increase of 2.8 °C. As for the mean annual temperatures, the average before and after the break equal to 18.85 and 21.13 °C, respectively, with a warming of 2.3 °C. For minimum annual temperatures, the average before and after the break is 5.66 and 8.14 °C, respectively, with an increase of 2.5 °C. The rupture date of the maximum and the mean temperature series are approximately the same and this could be explained by the fact that these two parameters exhibit the same evolution during the study period. As for the series of minimum temperatures, it presents an early break (1994). This could be explained by the very cold temperatures experienced by the study area in 1988, 1989 and 1990 (start of the series).

This upward trend is corroborated by the Mann-Kendall test with a positive multivariable standard normal $U_{MK}$ for annual maximum temperatures ($U_{MK} = +5.24$), for annual mean temperatures ($U_{MK} = + 5.65$) and annual minimum temperatures ($U_{MK} = + 4.65$).

The Gaussien diagram corresponds to the intersection of the monthly average precipitation curve and the monthly average temperature curve for the same station. When the precipitation curve is above that of
temperatures, we talk about a wet period. While the dry period takes place when the precipitation curve is below that of temperatures.

This diagram distinguishes a dry period from a wet period (Bagnouls and Gaussen 1953; Daget 1977; Hannachi and Fenni 2013). For this study and during the period 1987–2000, Figure 6 shows a dry period from April to September and a wet period from October to March. However, groundwater recharge could, therefore, take place mainly during this wet period. By comparing the length of the dry period during the two periods 1987–2000 and 2001–2014, we can see that it experienced an extension of about one month. This will undoubtedly influence the groundwater recharge.

**Piezometry**

The evolution of the groundwater piezometric surface is closely related to the variation of precipitation (Bahir et al. 2016; Ouhamdouch et al. 2016), the degree of exploitation and the contributions of surface water.

The piezometric maps drawn up from the data of September 1990, June 1995, March 1997, October 2007, June 2015, April 2016, April 2017, May 2018 and March 2019 companions for the aquifers of the Essaouira basin, show that:

- For the upstream part of the basin, the groundwater has a general flow direction from SE to NW for the southern part and from NE-SW for the northern part (Fig.7a). This flow is conditioned by the substratum of the reservoir studied. Over a 24-year observation period (1995–2019), the groundwater maintains the same direction of flow with a decline in the piezometric level. This drawdown is manifested, for example, by the offset of the piezometric curves 450 and 600 m more and more upstream, and this on the two piezometric maps (Fig.7a). Monitoring the evolution of the piezometric level of the wells whose water level was measured during October 2007, April 2016, April 2017, May 2018, and March 2019 is shown in the Figure 8. This shows that all of the wells have suffered a decline in their piezometric levels. It reached 9.3 m at well O30 and 12.6 m at well 75/52 between 2007 and 2019.

- For the downstream part, the general direction of groundwater flow of the Plio-Quaternary aquifer and that of the Barremian-Aptian is generally from south-east to north-west (Fig.7b and c). The groundwater flow within the Plio-Quaternary aquifer is imposed by the inclination of its substratum, while for the Barremian-Aptian, the flow is imposed by the north flank of the Amssittene anticline and the uplift of the substratum of the lower Cretaceous formations. Concerning the Hauterivian aquifer, the general direction of flow is from the northeast to the southwest and this follow the southern flank of the Amssittene anticline. The same remark observed for the downstream part, the groundwater keeps the same direction of the flow with a decline in the piezometric level. Over a 29-year observation period (1990–2019) (Fig.7b), the groundwater of the Plio-Quaternary aquifer keeps the same direction of flow with a decent piezometric level. This situation is materialized, for example, by the shift of the isopiezes 40 and 180 m more and more upstream, and this on the two piezometric maps. The evolution of the piezometric level of
the wells capturing this aquifer and having experienced measurements of their water body during 1990, 1995, 2000, 2004, 2009, 2015, 2017, 2018 and 2019 (Table 2) shows a reduction in the plan of water at these wells. It reached 17 m at well 261/51 and 6.6 m at well 140/51, between 1990 and 2019. The drought of 1995, the driest year in Morocco during the 20th century, led to a general decline in the water level.

Over a 43-year observation period (1976–2019) (Fig.7c), the groundwater of the Barremian-Aptian and Hauterivian aquifer keeps the same direction of flow with a decent piezometric level. With a total of nine wells, in which six wells capture the Barremian-Aptian aquifer and three captures the Hauterivian aquifer, having experienced measurements of their water body during 1976, 1997, 2015, 2017, 2018 and 2019, the study of the groundwater level of the aforementioned aquifers shows a decrease in piezometric levels (Table 3). For the Barremian-Aptien aquifer, it reached 9.1 m at well 176/51 and 8.8 m at well 173/51, between 1976 and 2019, i.e. an average annual decrease of 0.2 m. As for the Hauterivian aquifer, this reduction reached 4.8 m at the level of well P6 and 3 m at the level of well 193/51, i.e. an average annual decrease of 0.11 and 0.07 m respectively.

Following the absence of industrial activity in the study area and the agricultural activity of “food type” practiced by the population, the decrease in the piezometric level could only be explained by the decrease in precipitation under the effect of climate change.

Hydrogeochemistry

A hydrogeochemical approach is a valuable tool for characterizing groundwater chemistry. The latter is largely influenced by the characteristics of the host rock, the hydrodynamics of the aquifers and also by the climatic and exploitation conditions.

Chemical facies

To specify the groundwater chemical facies in the study area, the major element composition has been plotted on the Piper diagram (Piper 1944).

-For the Cenomanian-Turonian aquifer, representing the upstream part of the basin studied, the projection of the analysed samples on the Piper diagram (Fig.9a) shows that the waters have a mixed facies between Cl-Na, Cl-Ca-Mg, SO$_4$-Ca-Mg, and HCO$_3$-Ca-Mg. In 1995, the majority of the samples presented a Cl-Ca-Mg facies. For the samples of the 2007 campaign, the chemical facies of the waters are of Cl-Ca-Mg, SO$_4$-Ca-Mg and HCO$_3$-Ca-Mg type with the dominance of the Cl-Ca-Mg type. As for the samples analysed in 2016, they have a facies of Cl-Na type and of the Cl-Ca-Mg and SO$_4$-Ca-Mg type. For the 2017, 2018 and 2019 campaigns, we note that the analysed waters present three types of facies: Cl-Na, Cl-Ca-Mg, SO$_4$-Ca-Mg, and HCO$_3$-Ca-Mg with the dominance of the Cl-Ca-Mg type. A comparison of the results
of the 1995 campaign and those of 2019 (Fig.9b) shows that the groundwater facies of the Cenomanian-Turonian aquifer have not experienced any remarkable change.

For groundwater of the downstream part, the analysis of the Piper diagrams for the Plio-Quaternary and Turonian aquifers (Fig.10a and b) shows that they are classified under a mixed facies between Cl-Na and Cl-Ca-Mg. The regrouping of the points of the Plio-Quaternary aquifer near the Turonian aquifer suggests an interconnection between these two aquifers.

The comparison between the results of 1990 and 2019 is presented in Figure 10c. This shows that there is a slight evolution in the chemical facies of the Plio-Quaternary groundwater. Indeed, on the cations triangle concerning the 1990 campaign, the majority of the points have a percentage higher than 50% in Na\(^+\) with a tendency towards the Na pole. However, in 2019, the majority of the points do not exceed 50% in Na\(^+\) with a tendency towards the center of the sorting “no dominant cations”. For the anion triangle, a clear dominance of Cl\(^-\) is noted, whether in 1990 or in 2019. The position of certain samples relative to the sample representing seawater on the Piper diagram suggests that the Plio-Quaternary aquifer is probably affected by the marine intrusion.

The groundwater of the Barremian-Aptian and those of the Hauterivian generally present three types of chemical facies: Cl-Na, Cl-Ca-Mg, and HCO\(_3^-\)Ca-Mg with the dominance of the second facies (Fig.11a and b). The dominance of Cl over HCO\(_3^-\) could be explained by the influence of Triassic saliferous formations. The comparison between the water points sampled in 1997 and 2019 (Fig.11c) shows a remarkable evolution in the groundwater chemistry of the Barremian-Aptian and Hauterivian aquifers from the mixed facies Cl-Na and Cl-Ca-Mg to the facets Cl-Ca-Mg.

**Groundwater mineralization**

To determine the origin and the main processes responsible for the groundwater mineralization of the study area, the correlations between the main major elements have been studied.

Chloride is a conservative ion that is always found in natural waters at very variable contents (Fetter 1993) and sodium is generally associated with chlorides. Chlorides concentrations in groundwater of the upstream part vary widely from 113 to 1818 mg/l with an average of 574 mg/l. As for those of sodium, they vary between 12 and 541 mg/l with an average of 167 mg/l. According to the Piper diagram (Fig.9), it can be seen that the Cl\(^-\) ions are the most dominant in the waters. For the downstream part, the Cl\(^-\) contents vary between 120 and 4800 mg/l with an average of 620 mg/l and the Na\(^+\) concentrations vary between 28 and 1950 mg/l with an average of 261 mg/l. The highest Na\(^+\) and Cl\(^-\) contents are observed at the Plio-Quaternary aquifer.

The Na\(^+\) vs Cl\(^-\) correlation diagram (Fig.12a) shows a significant positive correlation between these two ions. This reflects that these two elements probably have the same origin. Some points are scattered around the halite dissolution line (line 1:1), reflecting the contribution of this mineral in the groundwater
mineralization of the study area. This hypothesis is confirmed by negative values of the saturation indices with respect to this mineral (Fig.13). The rest of the samples are located below the line 1:1 and parallel to it, reflecting a Na\(^+\) deficit. This suggests the contribution of a phenomenon other than the halite dissolution in the groundwater mineralization.

The Na\(^+\) deficit compared to Cl\(^-\) could be linked to the basic exchange reactions, as shown in the Figure 12f, with the aquifer matrix where the Na\(^+\) ions are released from the complex and are replaced by Ca\(^{2+}\) ions according to equation (1) (Capaccioni et al. 2005):

\[ \text{Na}^{++12}\text{Ca-X}_2 \rightarrow \text{Na-X}+12\text{Ca}^{2+} \] (1)

With X being the natural exchanger

Also, an excess of Na\(^+\) could be explained by the second type of cations exchange where the Ca\(^{2+}\) and/or Mg\(^{2+}\) ions will be released in water and the Na ions will be fixed by the matrix according to equation (2):

\[ 12\text{Ca}^{2+}+\text{Na-X} \rightarrow 12\text{Ca-X}_2+\text{Na}^+ \] (2)

The Ca\(^{2+}\) contents of the groundwater from the upstream part vary between 82 to 770 mg/l with an average of 214 mg/l. As for those of SO\(_4^{2-}\), they vary between 13 and 1942 mg/l with an average of 339 mg/l. As for the downstream part, the Ca\(^{2+}\) concentrations oscillate between 64 and 850 mg/l with an average of 158 mg/l and those of SO\(_4^{2-}\) vary between 30 and 830 with an average of 147 mg/l.

Figure 12b shows the existence of a significant correlation between the Ca\(^{2+}\) and SO\(_4^{2-}\) ions. Indeed, the points whose Ca\(^{2+}\)/SO\(_4^{2-}\) molar ratio is close to or equal to 1, reflect the same origin of these two ions which could be the dissolution of gypsum and/or anhydrite. This is confirmed by negative values of the indices of saturation with respect to gypsum and/or anhydrite (Fig.13). However, the excess of Ca\(^{2+}\) compared to SO\(_4^{2-}\) observed for the majority of the points could be linked to the phenomenon of reverse bases exchange. Also, the saturation indices calculated for these points with respect to carbonate minerals are close to or greater than zero, corroborating that the enrichment of Ca\(^{2+}\) is mainly due to the bases exchange (Fig.12f).

The Ca\(^{2+}\) vs Mg\(^{2+}\) diagram (Fig.12c) shows a positive correlation between these two ions, this reflects that these two elements come from the same origin. The majority of the points are scattered around the dolomite dissolution line (line 1:1), thus suggesting the contribution of the dissolution of this mineral to the groundwater mineralization. Other points are located above the line 1:1, confirming the contribution of the bases exchange process in the groundwater mineralization of the aquifers studied.
The Ca\(^{2+}\) vs HCO\(_3^-\) correlation (Fig.12d) shows that these two elements do not have a significant correlation and that the majority of the analyzed samples show a Ca\(^{2+}\)/HCO\(_3^-\) molar ratio greater than 1. This excess of Ca\(^{2+}\) compared to HCO\(_3^-\) ions translates the existence of other sources of calcium which could be the phenomenon of ion exchange and that of dedolomitization (incongruent dissolution of dolomite) (Marfia et al. 2004) accompanied by simultaneous precipitation of calcite.

**Nitrates contamination**

The main source of nitrate in water is the leaching of nitrogenous products in the soil following the decomposition of organic matter or synthetic and/or natural fertilizers. The nitrate content of unpolluted natural waters is highly variable, varying from 1 to 15 mg/l depending on the season and the origin (Chenaker et al. 2017).

The NO\(_3^-\) contents in groundwater of the Cenomanian-Turonian aquifer (upstream part) measured in March 2019 vary from 0 to 175 mg/l with a punctual spatial distribution (Fig.14a). Generally, levels are high in the Meskala region and exceed the threshold (50 mg/l) set by the World Health Organization (WHO 2011). Also, high values have been noted in some other wells such as 613/52 upstream O37 and 75/52 west of the Kourimat and O56 downstream.

For the Plio-Quaternary and Turonian aquifers, the NO\(_3^-\) contents vary, respectively between 0 and 400 mg/l and between 0 and 65 mg/l (Fig.14b). As for the Barremian-Aptian aquifer, it has NO\(_3^-\) contents varying between 5 and 60 mg/l. While the Hauterivian, has concentrations varying between 3 and 16 mg/l (Fig.14c).

The very weak correlation between Cl\(^-\) and NO\(_3^-\) (Fig.12e) makes it possible to say that the levels of NO\(_3^-\) assayed in the samples analyzed are not of agricultural origin since the chlorides are due to the dissolution of the evaporate minerals.

The highest concentrations within the Plio-Quaternary aquifer are recorded in the southwest part, near Cap Sim (wells 11/51, O94 and O95) and in the northwest; tourist area of the Diabate (well 149/51). These high levels could be explained by the intense concentration of septic tanks constructed by the guest houses in the tourist area of Sidi Kaouki because of the absence of a sanitation network. As for the Turonian and Barremian-Aptian aquifers, only two points for each aquifer have levels exceeding the limit set by WHO (2011). The high grades at well P5 (Barremian-Aptian aquifer) are caused by the public waste dump of the Smimou center because this dump is located a few meters from this water point. Regarding the Hauterivian aquifer, all the samples have NO\(_3^-\) concentrations of less than 50 mg/l. The low NO\(_3^-\) concentrations in Hauterivian aquifer compared with the other aquifers could be explained by a low concentration of the population in this zone.
The contamination (<50 mg/l) of the other wells at the level of the aquifers studied could be explained by 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 $\text{NO}_3^-$ by livestock waste during watering. Note also that the number of contaminated wells in the Plio-Quaternary and Turonian aquifer (northern part of the downstream part) is greater than that of the Barremian-Aptian and Hautarivian aquifers (southern part of the downstream part). This is mainly due to the concentration of inhabitants in the northern part, where the water points are located in the middle of the agglomerations, while in the southern part and because of highly uneven geology, most wells are far from the places habitat.

**Evolution of groundwater salinity**

The groundwater salinization is a very marked phenomenon in areas of water scarcity, especially the Saharan, arid and semi-arid zones. The scarcity or even the absence of surface water and the increasing demand for water as well as the decrease in precipitation have created enormous pressures on groundwater which have thus resulted in the degradation of their quality.

The spatial-temporal distribution of salinity was studied to assess the impact of climate change on the groundwater quality by using the results of the campaigns of 1995, 2007, 2016, 2017, 2018, and 2019. For the upstream part, the 1995 campaign shows the salinity values vary between 0.2 and 1.9 g/l with an average of 0.7 g/l. In 2007, the salinity values fluctuated between 0.5 and 2.4 g/l with an average of 1.1 g/l. As for the 2016 campaign, its values vary between 0.3 and 4.6 g/l with an average of 1.37 g/l. For the 2017 campaign, the salinity fluctuates between 0.3 and 4 g/l with an average of 1.29 g/l. In 2018, the salinity values vary between 0.4 and 4.3 g/l with an average of 1.4 g/l and between 0.35 and 4.4 g/l with an average of 1.4 for samples from the 2019 campaign (Fig.15).

From the analysis of the maps in Figure 15, it can be seen that the salinity values become more important by advancing in time and going from east to west and this during the six campaigns. Taking, for example, the region of Sebt Kourimat, recharge area of the Cenomanian-Turonian aquifer, the salinity values fluctuate around 0.46 g/l in 1995 to reach 2.9 g/l in 2019. However, the general spatial-temporal evolution of salinity shows an increasing trend.

For the downstream part, the groundwater from the Plio-Quaternary aquifer has salinity values varying between 0.6 and 3.4 g/l with an average of 1.7 g/l in 1990, between 0.9 and 3 g/l with an average of 1.6 g/l in 1995, from 0.4 to 4.1 g/l with an average of 1.3 g/l in 2004, between 0.9 to 2.2 g/l with an average of 1.4 g/l in 2009, from 0.3 to 4.7 with an average of 1.5 g/l in 2015, between 0.4 and 4.8 g/l with an average of 1.53 g/l in 2017, between 0.5 and 6.5 g/l with an average of 1.6 g/l in 2018 and between 0.46 and 8.4 g/l with an average of 1.7 g/l in 2019 (Fig.16). From the maps of Figure 16, the highest values are observed in the southern and western part and this further to the remoteness to the recharge zones, to the residence time, to the influence of the Triassic terrains, and to the influence from the sea (marine intrusion (well 11/51)). While the low values of salinity are recorded in the north (along the Ksob wadi) and in the east of the Plio-Quaternary aquifer which represent the recharge zones. These low values are
due to the fact that these places represent the recharge zones of this aquifer. The temporal evolution of groundwater salinity of the Plio-Quaternary aquifer shows an upward trend going from year to year and consequently deterioration in the groundwater quality. As for the Turonian aquifer, the minimum values of salinity are around 0.8 g/l and the maximum values are around 1.3 g/l with an average of 1.1 g/l, and this for 2004, 2009, 2015, 2017, 2018 and 2019 campaigns (Fig.16). The temporal evolution of the groundwater salinity of this aquifer does not show a significant trend, this could be explained by its significant depth and its captive nature.

Concerning the Barremian-Aptian aquifer, the salinity values vary between 0.2 and 3.2 g/l with an average of 1.1 g/l for the points representing the 1997 campaign, from 0.3 to 2.1 g/l with an average of 1.1 g/l for the samples collected in 2015 and 2017, between 0.4 to 2.8 g/l with an average of 1.1 g/l for the points of 2018 campaign waters and between 0.7 and 2.4 g/l with an average of 1.2 g/l for 2019 campaign (Fig.17).

The spatial-temporal distribution of the groundwater salinity of the Barremian-Aptian aquifer (Fig.17) shows a slight upward trend in the minimum values of the salinity while the maximum values have experienced slight stability. For the Hauterivian aquifer, the salinity values vary between 0.6 to 2.6 g/l with an average for waters representing the 1997 campaign, between 0.5 and 1.1 g/l with an average of 0.8 g/l for the 2015 samples, between 0.6 to 1.2 g/l with an average of 0.9 g/l for the points of the 2017 campaign, between 0.4 and 1.1 g/l with an average of 0.8 g/l for the 2018 campaign and between 0.4 to 1.3 g/l with an average of 0.8 g/l for the 2019 samples. The spatial-temporal distribution of the salinity of the Hauterivian aquifer shows a slight dilution of the waters analyzed in 2015, 2017, 2018 and 2019 compared to those representing the 1997 campaign. This could be explained by the installation of the Igouzoullene dam (in 2004) in upstream favoring the recharge of this aquifer.

As the study area is under a semi-arid climate, with a tendency towards an arid climate in recent years accompanied by a decrease in precipitation and an increase in the temperature, which frequently causes intense periods of drought resulting in evaporation that affects surface and groundwater, especially the shallow waters, the degradation of the groundwater quality is mainly due to this situation and the decrease in the piezometric level caused by climate change.

**Isotopy**

The isotopic approach is of crucial importance in studies of aquifer systems. They make it possible to determine the groundwater origin and their residence times, to identify and quantify the rate of mixing between two types of water and to locate the recharge areas (Fontes 1976).

For the upstream part (Cenomanian-Turonian aquifer), the oxygen$^{18}$ contents vary between a minimum of $-6 \text{‰ vs SMOW}$ and a maximum of $-3.3 \text{‰ vs SMOW}$, with an average of $-4.9 \text{‰ vs SMOW}$. For deuterium, the maximum value is $-20.2 \text{‰ vs SMOW}$ and the minimum value equal to $-34.5 \text{‰ vs SMOW}$ with an average of $-28.4 \text{‰ vs SMOW}$ (Appendix 2). As for the downstream part, the contents of
oxygen–18 vary between a minimum of –5 ‰ vs SMOW and a maximum of –1.8 ‰ vs SMOW, with an average of –3.9 ‰ vs SMOW for the Plio-Quaternary aquifer and between a minimum of –5 ‰ vs SMOW and a maximum of –4.4 ‰ vs SMOW, with an average of –4.7 ‰ vs SMOW for the Turonian aquifer. For deuterium contents, the maximum value is –8.9 ‰ vs SMOW and the minimum value equal to –29.7 ‰ vs SMOW with an average value of –22.6 ‰ vs SMOW for the Plio-Quaternary layer. As for the Turonian, the maximum value is –27.3 ‰ vs SMOW and the minimum value equal to –28.5 ‰ vs SMOW with an average value of –27.9 ‰ vs SMOW (Appendix 2). The comparison of the stable isotope contents of the upstream part and the downstream part of the Essaouira basin shows a slight depletion of the waters of the upstream part compared to those of the downstream part in these isotopes. This is due to the effect of elevation and continentality due to the remoteness of the coast.

In the absence of a local meteorological line characterizing the isotopic composition of the rainwater in the study area, the meteoric line with equation $\delta^2H = 7.95 \times \delta^{18}O + 11.3$ was considered by Mennani et al. (2001) as an input function for the aquifer systems of the Essaouira basin. Figure 18, representing the variation of $\delta^2H$ vs. $\delta^{18}O$ of the groundwater representing the Cenomanian-Turonian aquifer, shows that some samples are located above the global meteoric water line (GMWL) and around the local meteoric water line (LMWL). This reflects that the aquifer recharge is ensured by the infiltration of precipitation of oceanic origin without significant evaporation. While some points are located below GMWL suggesting that these points have evaporated before being infiltrated to the aquifer. The sample of precipitation is an annual average of samples collected in 2004, 2006, 2016 and 2018. As for the seawater sample, we refer to values obtained by Carreira et al. 2014.

The distribution of representative samples of the groundwater representing the Plio-Quaternary and Turonian aquifers (downstream part) on the correlation diagram $\delta^2H$ vs $\delta^{18}O$ (Fig.18) shows that the majority of the points are scattered around the GMWL and LMWL reflecting a recharge by infiltration of oceanic rainwater (Group1). This supply of the shallow aquifer by rainwater, which is at the origin of the reduction in the salinity of the waters in these wells, is in perfect agreement with the hydrogeochemical data, in particular, well 27/51 which has low salinity. This well is the closest to the freshwater pole. Other local recharge points for rainwater have been identified in the bowl of the Essaouira basin (example O6, 15/51). This recharge is probably favored by the lithological nature and the small thickness of the unsaturated zone. This group contains both the majority of the samples representing the shallow Plio-Quaternary aquifer and all the water points representing the deep Turonian aquifer. This suggests the existence of a connection between these two aquifer systems.

Other water points are distinguished by their position below the GMWL (Group 2), they line up along a line with a slope less than 8 characteristics of evaporation phenomenon. This last process mainly concerns surface waters (O98 and O99) and wells 105/51 and 327/51 located respectively in the northeast and south part of the aquifer (Fig.18). Evaporation can probably take place before water infiltration, in the unsaturated zone or during sampling. In the same diagram, well 11/51 is aligned on the freshwater-seawater mixture line. This confirms that the increase in mineralization in this well is caused by the phenomenon of marine intrusion.
Following the availability of Tritium data, only the Cenomanian-Turonian aquifer was the subject of the groundwater dating in the study area. However, the tritium contents vary between 0 and 2.1TU. The highest values were recorded in the Et Tleta Hanchane region and the Kourimat region. This confirms that the recharge of the aquifer through rainwater is low and limited to a few regions (Fig.19). According to Mazor (1991), a tritium content greater than 1 TU indicates a post-nuclear recharge and content less than 1 TU represents a pre-nuclear recharge or a mixture between recent and old waters. The high tritium levels have been observed in the Kourimat and Et Tleta Hanchane region (recharge zone), and they can be attributed to the recent infiltration of precipitation.

The projection of the samples from the two 2016 and 2007 campaigns (Fig.19) shows that certain points are located above the line 1 TU reflecting a recent recharge of the Cenomanian-Turonian aquifer, while the other points are located above below this line confirming a pre-nuclear recharge. A comparison of the $^3$H content of the same water point sampled in 2007 and 2016 shows a decrease in the $^3$H content. This decrease could be explained by the low recharge rate caused by the decrease in the precipitation rate, which the study sector has experienced in recent decades under the effect of climate change.

To get an idea on the evolution of $^{18}$O contents of groundwater in the context of climate change, we have based on the two Plio-Quaternary and Turonian aquifers where we have monitoring of the isotopic signature. The results are grouped in Figure 20. The correlation diagram $^{18}$O-$^2$H for each point during the 23-year (1995–2018) shows that the recharge of the Plio-Quaternary and Turonian aquifers is ensured by precipitation of oceanic origin without notable evaporation. Only two points are located below the GMWL, it is point 272/51 (in 2004) and point 11/51 (in 2018). This situation could be explained by the fact that point 272/51 underwent evaporation before infiltration, while point 11/51 underwent marine contamination as shown in Figure 21 where the electrical conductivity is around 10 mS/cm. According to Figure 21 we see that the increase in electrical conductivity (salinity) is accompanied by a very small increase in the $^{18}$-oxygen contents. This slight enrichment in $^{18}$O (1 to 1.5 ‰), may be due to the effect of evaporation caused by the increase in air temperature under the effect of climate change. This suggests that the isotopic content of the study area is impacted by climatic variations and therefore it can be concluded that global warming has an effect on the isotopic signature of groundwater within the Essaouira basin.

**Conclusion**

The water resource within the Essaouira basin is limited and unevenly distributed in space and time. This problem could limit water supply, which will be aggravated by the depletion of this resource due to the climate change impact which has become an ambiguous reality and whose effects on the environment are already visible.

The combination of hydroclimatic, piezometric, hydrogeochemical and isotopic approaches in the study of the groundwater resource within the Essaouira basin led to the following conclusions:
The analysis results of the annual precipitation time series using the statistical tests, in particular, that of Pettitt and that of Mann-Kendall, made it possible to detect a decrease in precipitation in the whole basin of 12 to 16%. This decrease in precipitation is accompanied by an increase in temperatures with a significant extent of warming of 2.3 °C. Based on the Gausseen diagram, the comparison of the duration of the dry period for the two periods 1987-2000 and 2001-2014 shows an extension of one month. This will no doubt have a negative effect on the groundwater recharge.

The piezometric approach has shown that the Cenomanian-Turonian, Plio-Quaternary, Barremian-Aptian and Hauterivian aquifers have retained the general direction of flow of their groundwater, during the study period. Monitoring the piezometry over a period of 24 years (1995-2019) for the Cenomanian-Turonian aquifer, 29 years (1990-2019) for the Plio-Quaternary aquifer and 43 years (1976-2019) for the aquifers Barremian-Aptian and Hauterivian shows a continuous drop in the piezometric level which exceeds 12 m for the Cenomanian-Turonian aquifer, 17 m for the Plio-Quaternary aquifer, around 8 m for the Barremian-Aptian aquifer and 5 m for the Hauterivian.

The general decline in the piezometric level could be explained by the decrease in precipitation following the harmful effect of climate change. This drawdown would probably cause a qualitative degradation of groundwater.

The hydrogeochemical study showed that the groundwater of the Cenomanian-Turonian aquifer presents the Cl-Ca-Mg, Cl-Ca, Cl-Na, and HCO₃-Ca mix facies with the dominance of the Cl-Ca-Mg mix facies, and Cl-Ca. The study of the temporal evolution of these facies shows that there has been no remarkable change. The groundwater of the Plio-Quaternary and Turonian aquifers are of mixed type between Cl-Na and Cl-Ca-Mg. The chemical facies experienced a slight evolution from the Cl-Na facies to the Cl-Na and Cl-Ca-Mg facies for the Plio-Quaternary aquifer and from the Cl-Na facies to the Cl-Ca-Mg facies for the Turonian aquifer. As for the Barremian-Aptian and Hauterivian aquifers, they generally have three types of chemical facies: Cl-Na, Cl-Ca-Mg, and HCO₃-Ca-Mg, with the dominance of the Cl-Ca-Mg facies. For the study period, a remarkable evolution of the facies was observed; from the Cl-Na facies to the Cl-Ca-Mg facies.

Examination of the correlations established between the concentrations of major elements has shown that the mineralization of groundwater is controlled by the phenomenon of the dissolution of the evaporitic minerals (halite, gypsum and/or anhydrites) and carbonates (dolomite), by the reverse ion exchange phenomenon and by the marine intrusion, especially at the Plio-Quaternary aquifer. The study of the spatio-temporal evolution of the groundwater quality in the study area shows a gradual deterioration in time and space.

The tracing of the groundwater in the Essaouira basin by stable isotopes has shown that the groundwater recharge in the upstream part of the basin studied is ensured by precipitation of Atlantic origin without significant evaporation. The same method of recharging is marked at the downstream part, with this time the presence of contamination by seawater.
Tritium tracing based on the same wells sampled in 2007 and 2016 shows a significant decrease that reaches 2 TU in certain wells. This trend could be explained by the low recharge rate following the decrease in the precipitation rate experienced by the study area in recent years. The temporal evolution of the $^{18}$O contents generally shows slight enrichment of 1 to 1.5 $\%$, this may be due to the effect of evaporation caused by the increase in air temperature under the effect of climate change.

However, the Essaouira basin is more vulnerable to climate change because its recharge is entirely dependent on meteoric waters.

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**Availability of data and materials**

Please contact author for data requests

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**Competing interests**

The authors declare that they have no competing interests.

**Authors' contributions**

MB and SO prepare figures and maps and analyzed the data, DO helped in the interpretation. NE collaborated with the corresponding author in the construction and submission of manuscript. All authors read and approved the final manuscript.

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Figures

Figure 1

Location of study area
Figure 2

Geological map of study area and cross sections location
Figure 3

cross sections (cf Figure 2)
Figure 4

(a) Annual precipitations  (b) Pettitt test result
Figure 5

(a) Maximum, average and minimum temperatures, (b) Pettitt test results
Figure 6

Gaussen diagram
Figure 7

Piezometric maps of the aquifer (a) Cenomanian-Turonian (b) Plio-Quaternary and (c) Barremian-Aptian and Hauterivian
Figure 8

Temporal evolution of the piezometric level of certain wells capturing the Cenomanian-Turonian aquifer
Figure 9

Piper Diagram of analysed samples of (a) Cenomanian-Turonian aquifer from 1995 to 2019 and (b) comparison between samples of 1995 and 2019
Figure 10

Piper Diagram of analysed samples of (a) Plio-Quaternary from 1990 to 2019 and of (b) Turonian from 2009 to 2019, and (c) comparison between samples of 1990 and 2019 for the Plio-Quaternary aquifer
Figure 11

Piper Diagram of analysed samples of (a) Barremian-Aptian and (b) Hauterivian aquifers from 1997 to 2019, and (c) comparison between samples of 1997 and 2019 for the two aquifers
Figure 12

Correlation diagram (a) Na vs Cl, (b) Ca vs SO₄, (c) Ca vs Mg, (d) Ca vs HCO₃, (e) NO₃- vs Cl, and (f) (Ca+Mg+HCO₃-SO₄) vs (Na+K-Cl)
Figure 13

Saturation indices of analysed samples of (a) Cenomanian-Turonian, (b) Plio-Quaternary, (c) Turonian, (d) Barremian-Aptian, and (e) Hauterivian aquifers
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Spatial distribution of NO3- content in groundwater of (a) Cenomanian-Turonian, (b) Plio-Quaternary and Turonian, and (c) Barremian-Aptian and Hauterivian aquifers
Figure 15

Spatial distribution of salinity in Cenomanian-Turonian aquifer
Figure 16

Spatial distribution of salinity in Plio-Quaternary and Turonian aquifers
Figure 17

Spatial distribution of salinity in Plio-Quaternary and Turonian aquifers
Figure 18

Spatial distribution of salinity in Barremian-Aptian and Hauterivian aquifers
Figure 19

$\delta^2\text{H}-\delta^{18}\text{O}$ correlation diagram of the groundwater of (a) the Cenomanian-Turonian aquifer and (b) the Plio-Quaternary and Turonian aquifers
Figure 20

Relation oxygen-18 and tritium content of Cenomanian-Turonian groundwater

Figure 21

Isotopic contents evolution of the groundwater of the Plio-Quaternary and Turonian aquifers
Figure 22

Evolution temporal of $^{18}$O content and Electrical Conductivity of points capturing Plio-Quaternary and Turonian aquifers

Supplementary Files

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- GraphicalAbstractImagerevised.docx