

HYDROGEOCHEMICAL CHARACTERISTICS OF PROCESSES IN THE TEMARA AQUIFER IN NORTHWESTERN MOROCCO

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Abstract. The physico-chemical characteristics of the groundwater of the Temara aquifer were studied by means of piezometric mapping and determination of the ionic composition of the groundwater. In general, the agricultural activity is intense in the area, with water being pumped from numerous wells. Two aquifer formations can be distinguished which, over a wide area, are separated by layers of low permeability. The increased salinity at some points of the coastal zone is probably linked to the combined action of the washing out of Miocene marls, dissolution of carbonate rocks, agricultural pollution and seawater intrusion.

Keywords: agricultural activities, groundwater quality, hydrogeochemistry, ionic ratios, pollution, pumping

1. Introduction

The use of water from the Temara aquifer in northwestern Morocco is mainly dedicated to agricultural irrigation and human consumption. The economically valuable crops are predominantly table vegetables, legumes, cereals, trees and forage crops. The exploitation of the aquifer, coupled with the drought prevailing in Morocco for the last decade, has caused a fall in the piezometric levels – between 1968 and 1994 falls of over 20 metres have been measured in the Ain Reboula area – , accompanied by a rise in salinity in the southwestern coastal area (Tahiri and Pulido-Bosch, 1996). This situation has forced the farmers in the Ain Reboula area to abandon their wells and drill others upgradient in the hope of finding less saline water.

The main aim of this work is to characterize the hydrogeochemical processes that have produced a series of water types, with reference to phenomena which have the potential to modify the natural chemistry of the water (for example, relative changes in level between ocean and continent). The study area has a marked human influence and a complex recent geological history.



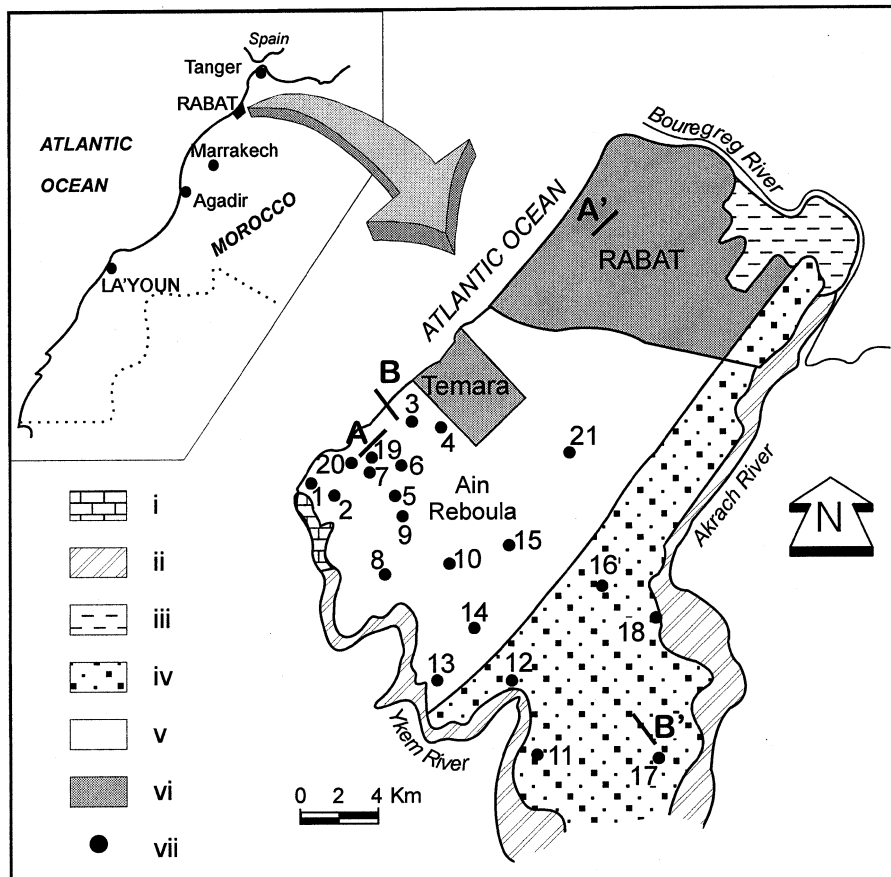


Figure 1. Geological scheme with situation of the principal wells; i: Devonian calcareous reef; ii: Carboniferous phyllites and schists; iii: Miocene marls; iv: Pliocene Sands and gravels; v: Quaternary formations; vi: urban areas; vii: well; AA' and B-B': representative cross-section (see Figure 2).

2. Materials and Methods

2.1. SITE DESCRIPTION

The study zone occupies part of the northwestern Moroccan Meseta (Piqué, 1979) which, between the Atlantic Ocean and the Moroccan Central Massif, constitutes a group of low plateaus sloping towards the coast, with an altitude not exceeding 300 m. The surface area of around 315 km² is bordered to the northeast by the Bouregreg River, to the east by its tributary Akrach, to the south and southwest by the Ykem River, and to the northwest by the Atlantic Ocean (Figure 1). The center of the area is situated 6 km south of Rabat.

The regional climate is semi-arid to temperate. The annual rainfall averages 530 mm (weather station at the Rabat-Salé Airport, for the period 1948–1993). The average annual temperature registers 17.2 °C and the actual evapotranspiration is 450 mm yr⁻¹, while the potential evapotranspiration is 885 mm yr⁻¹ (Thornthwaite method). These values were obtained during the same measurement period, 1948–1993.

The study area comprises two well-differentiated geological entities: the Palaeozoic substratum and the Miocene-Pliocene-Quaternary cover (Figure 1). The Palaeozoic substratum is composed of Devonian calcareous reef massifs which outcrop in the mouth of the Ykem River, and Carboniferous pelitic formations of phyllites and schists (Piqué, 1979). The cover was deposited by transgression over the folded Palaeozoic formation.

At the bottom of the Miocene materials, there is a 5 to 6 m thick layer of biotrital sands of Messinian age (Wernli, 1977). Above, there is marl of marine origin, which is about 90 m thick in the northeast of the study area, but gradually decrease towards the southwest until it disappears near the Ykem River valley (Figure 2, cross-section A-A'). During the Pliocene, marl deposition continued in the central and northern zones, whereas in the eastern zone, sands and gravels were deposited (Figure 2, cross-section B-B'). The Quaternary marine formations begin with a 1 m deposit of the Magreb flagstone composed of a coarse biotrital sandstone with cross-stratification. A deposit of calcarenites of about 15 to 20 m thickness covers this layer. Continental Quaternary formations of sands and red silts cover a large part of the study area, constituting fertile soils.

The material comprising the aquifers are Miocene biotrital sands and Plio-quaternary calcarenites, sands and gravels with a limestone-dolomite composition (see Figure 2), separated by Miocene marls whose thickness increases inland.

2.2. PIEZOMETRIC MAPPING

The piezometric map of the Temara aquifer (Figure 3) was drawn from measurements obtained at 220 points covering virtually all the aquifer. Groundwater flows from the SE towards the NW.

2.3. WATER SAMPLING

A water sampling survey was performed in October 1994 at twenty-one points covering most of the aquifer. The wells were installed with a slotted screen of at least several meters length and the water was extracted using a submersible pump from 10 to 15 meters below the water surface. Samples were collected after fifteen minutes pumping.

2.4. PHYSICO-CHEMICAL ANALYSES

Water analyses were carried out using standard procedures. However, some aspects deserve special comment concerning the collection and conservation of water samples, and the evaluation of the quality of chemical analyses deserve some special attention. Field analyses were made for the parameters pH, temperature (T), EC (Electrical Conductivity), which were all measured by electrode. A WTW Model pH-320 portable pH/temperature meter was used with a combination electrode. The meter was calibrated with buffer solutions at pH 7.00 and 10.00. EC measurements are particularly useful as a check on the analysis and conservation of samples. A WTW Model LF-320/SET conductivity meter was used for this parameter at 25 °C. The alkalinity of water samples was determined in the field by titration with HCl 0.05 N.

The other parameters were analyzed in the laboratory after transport in polyethylene bottles, stored at 4 °C and protected against the light. Ca, Mg, Na, K and Sr were conserved in the field by adding HNO₃ to the sample to achieve a pH of < 2 and determined by atomic absorption spectrophotometry (Perkin Elmer, model 2380). Sulphate was measured by ultra-violet light spectrophotometry. Chloride and nitrate were determined using a Dionex Ion Chromatograph with a standard calibration curve prepared from peak area measurements. The analysis of salt water was carried out on a volume base (by pipetting and diluting volumina), and recalculated to convert the results to concentration by weight.

Precision was calculated by repeated analyses of the same sample and the accuracy of the analysis for major ions was estimated from electroneutrality condition, where cations (Ca, Mg, Na and K) and anions (bicarbonate, chloride, sulphate and nitrate) were expressed as equivalents. At deviations of more than 5%, the sampling and analytical procedures were checked.

2.5. SALINITY ORIGIN TRACING

In attempting to identify the origin of the salinity in the area, the following ionic relationships were studied. These comprise Mg/Ca, Cl/HCO₃, the Cationic Exchange Value ($CEV = [Cl - (Na + K)] / Cl$), sulphate vs chloride, Ca vs chloride, Ca vs bicarbonate, Mg vs chloride, and Mg vs bicarbonate.

The Maturity Index (MI) of groundwater provides an indication of the residence time of the waters within the aquifer and is calculated from $MI = \Delta Sr / \Delta (Ca + Mg)$ (Pulido-Bosch *et al.*, 1995). Tulipano and Fidelibus (1991) proposed choosing water with low concentrations of Ca, Mg and Sr as a reference sample. Thus, for each sample, the ΔSr is calculated as the Sr content of the sample minus the Sr content of the reference sample, and likewise for $\Delta (Ca + Mg)$. High values should indicate a long residence time (fossil waters) and so indicate that water-rock interactions are important (Pulido-Bosch *et al.*, 1995).

The parameters affecting chemical equilibrium were calculated by means of the program WateqB (Trusdell and Jones, 1974; Plummer *et al.*, 1976; Arikian, 1988;

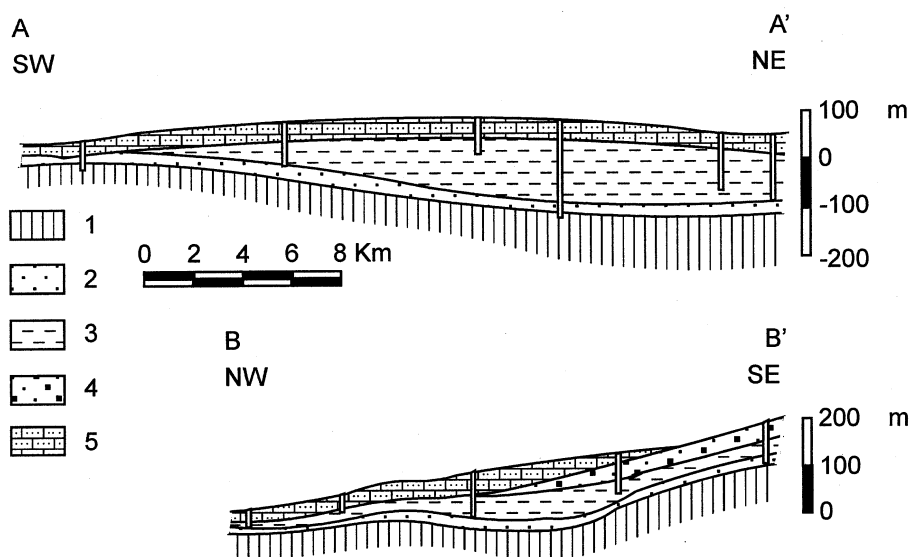


Figure 2. Geological cross-section: 1: substratum; 2: Messinian biodetrital sands; 3: Miocene marls; 4: Pliocene sands and gravels; 5: Quaternary calcarenites (see situation on Figure 1).

Appelo and Postma, 1993). Determination of the equilibrium states between water and the different solid phases was carried out by calculating the products of ion activity and solubility and by calculating saturation indices. The Debye-Hückel equation was used to determine the coefficient of activity of each ionic species since the waters were relatively dilute. In order to show the equilibrium states of the aquifer waters, five points were chosen on the flow line to illustrate the processes between the recharge zone and the discharge zone.

3. Results and Discussion

3.1. PIEZOMETRIC CHARACTERISTICS

Three well-differentiated groundwater sectors were identified (see Figure 3). The sector furthest from the sea shows a marked hydraulic gradient (average 1.2%), with an extreme value of 2%. This is followed by a central sector where the hydraulic gradient is considerably less (average 0.42%). This may possibly be due to the influence of pumping, as well as the fact that permeability values are higher in this area. Subsequently, there is a slight increase towards the coast, with an average value of 0.8%. Groundwater flow within the study area is from SE to NW. Thus, taking into account the total length of the aquifer along the direction of flow, together with the difference in piezometric levels, an average hydraulic gradient of 0.83% is obtained. The potentiometric lines are generally perpendicular to the

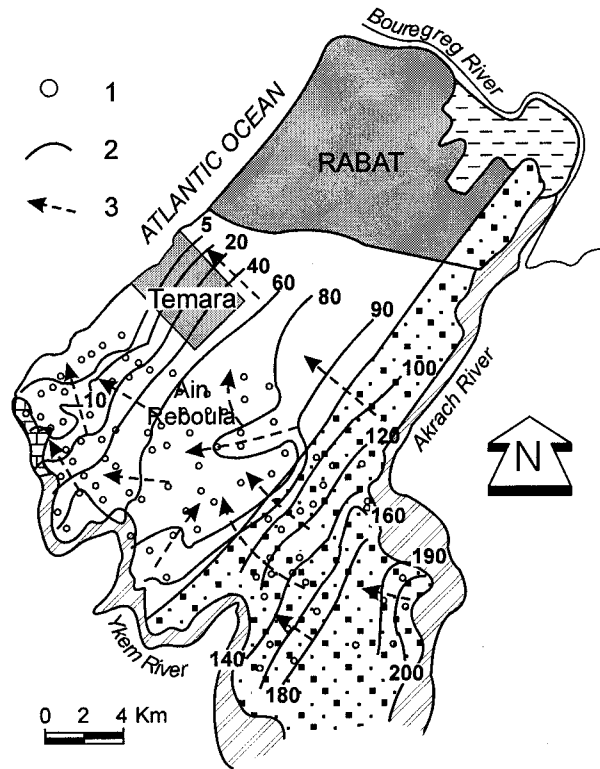


Figure 3. Piezometric scheme of the Temara aquifer (January 1994); 1: well; 2: potentiometric line (m a.s.l.); 3: flow direction.

river courses and parallel to the coastline, indicating that the ocean constitutes the drainage area on the western border.

3.2. PHYSICO-CHEMICAL CHARACTERISTICS

The conductivity values (Table I) were generally below $2000 \mu\text{S cm}^{-1}$, except in the southwestern coastal zone where higher values were measured for the points 7 and 20. At these two points, the content of the main ions were particularly high, with the exception of bicarbonate and Sr for point 7, and bicarbonate, nitrate and K for point 20.

There are several possible explanations for the variations in groundwater composition. Natural variations include the ionic input from rainwater, the chemical composition of the soil and processes occurring through the unsaturated zone. Other factors are due to human activity and include agriculture, water use, and sea-

TABLE I

Concentrations of chloride, sulphate, bicarbonate, nitrate, Na, Mg, Ca, K, Sr (meq l⁻¹), pH, temperature (T: °C) and electrical conductivity (EC: $\mu\text{S cm}^{-1}$) in twenty-one water samples from the Temara aquifer (October 1994)

N°	T	pH	EC	Cl	SO ₄	HCO ₃	NO ₃	Na	Mg	Ca	K	Sr
1	21.4	7.4	1500	6.76	0.83	3.00	0.30	5.65	1.71	2.69	0.08	0.007
2	21.1	7.4	1200	4.51	0.23	2.45	0.43	2.60	1.23	3.84	0.04	0.014
3	20.9	7.1	1300	5.10	1.48	3.00	0.80	3.91	1.80	3.64	0.03	0.011
4	21.2	7.0	1100	3.41	0.70	3.19	0.29	3.13	0.98	4.00	0.02	0.007
5	20.5	6.9	1400	7.89	0.80	3.59	0.61	4.30	2.63	5.00	0.05	0.011
6	20.9	7.2	1100	3.00	0.82	3.39	0.32	2.26	1.15	5.00	0.03	0.005
7	20.8	7.2	3300	11.41	6.97	3.19	2.12	6.95	4.68	10.97	0.08	0.018
8	21.6	7.3	1100	4.00	0.80	6.00	0.15	5.43	2.87	2.49	0.06	0.007
9	20.9	7.2	1600	3.61	1.66	2.87	1.10	2.21	3.78	3.68	0.00	0.023
10	20.7	7.1	1500	6.00	1.23	2.79	0.90	4.78	1.15	4.00	0.02	0.007
11	21.0	7.3	600	1.40	0.92	2.00	0.03	2.17	0.90	1.19	0.06	0.002
12	21.3	7.4	600	1.00	1.41	1.88	0.14	0.91	0.49	2.59	0.04	0.002
13	21.2	7.3	1100	4.80	1.66	4.27	0.12	3.13	2.71	3.49	0.05	0.007
14	21.2	6.9	700	2.03	1.70	4.26	0.13	2.39	0.98	3.34	0.02	0.002
15	20.8	7.2	1100	1.26	0.89	6.00	0.13	4.13	1.39	4.49	0.04	0.007
16	20.8	6.9	900	2.39	0.74	5.39	0.20	2.60	1.15	5.00	0.02	0.005
17	21.2	7.0	1300	5.41	3.41	4.19	0.25	6.74	3.45	4.84	0.03	0.005
18	21.2	6.9	2000	9.30	1.95	4.99	0.30	8.83	2.30	5.63	0.05	0.011
19	20.3	7.1	1200	4.80	1.00	3.79	0.79	3.39	2.30	3.49	0.03	0.007
20	20.9	6.8	10600	84.71	10.18	2.59	0.87	58.72	17.68	19.86	0.05	0.064
21	19.9	6.9	800	2.00	2.05	4.70	0.03	2.39	0.90	5.73	0.01	0.007

TABLE II
Hydrogeochemical indices Mg/Ca, Cl/HCO₃ and CEV (Cationic Exchange Value = [Cl-(Na+K)]/Cl) in water samples spread over the Temara aquifer (October 1994)

N°	Mg/Ca	Cl/HCO ₃	CEV
1	0.64	2.25	0.15
2	0.32	1.84	0.41
3	0.49	1.70	0.23
4	0.25	1.07	0.08
5	0.53	2.20	0.45
6	0.23	0.88	0.24
7	0.43	3.58	0.38
8	1.15	0.67	-0.37
9	1.03	1.26	0.39
10	0.29	2.15	0.20
11	0.76	0.70	-0.59
12	0.19	0.53	0.05
13	0.78	1.12	0.34
14	0.29	0.48	-0.19
15	0.31	0.21	-2.31
16	0.23	0.44	-0.10
17	0.71	1.29	-0.25
18	0.41	1.86	0.05
19	0.66	1.27	0.29
20	0.89	32.71	0.31
21	0.16	0.43	-0.20

water intrusion when the equilibrium is disturbed at the contact between freshwater and saltwater.

3.3. GROUNDWATER ORIGIN

Mg/Ca values measured were all less than 1.5 (Table II). The lowest value 0.16 was found at point 21 (northeast zone) and the highest 1.15 at point 8 (central zone). According to the interpretation of this index, the water in the study zone appears to be of inland origin, because waters under marine influence would have values of about 5 (Morell *et al.*, 1986) except where other processes such as cationic exchange intervene when the values could be 4 or less.

The Cl/HCO_3 values (Table II), ranged from 0.21 at point 15 (central zone) to 32.71 at point 20 (coastal zone). Values of this hydrogeochemical index given for inland waters are between 0.1 and 5 and for sea water between 20 and 50 (Custodio, 1987). Thus, the value of > 30 for point 20 (Table II) might be explained as the effect of seawater at this point, though in fact, other processes could produce the same result. Such would be the case of marine origin sediments that had not been completely flushed by the waters initially saturating them (fossil waters).

In general, the CEV for seawater range from +1.2 to +1.3 (Custodio, 1983), whereas low-salt inland waters give values of close to zero, either positive or negative. The waters from the Temara aquifer also gave values close to zero (Table II), ranging from -2.31 to 0.45 . The increase in groundwater salinity was accompanied by a slow rise in ionic exchange, which indicates a cationic exchange that increases the hardness of these waters. A decrease would indicate the opposite.

The value of the Cl/HCO_3 hydrochemical index for point 20 – coastal zone – shows that this point could be affected by seawater. We presume that the aquifer waters are undergoing mixing between fresh and seawater. Highly useful in identifying other phenomena which are subsidiary to the mixing processes could be a study of the relationships between the concentration of chloride (a conservative ion) and the concentrations of sulphate, Na, Mg, Ca, as well as a study of distribution of the different points with respect to the theoretical mixing line of freshwater and seawater. Consequently, different seawater samples were analyzed. The average composition of seawater samples thus found, together with that of aquifer water with the lowest saline content, was used to calculate the theoretical freshwater-seawater mixing line.

The sulphate vs chloride graph (Figure 4a) indicates that only one point (point 7 in the coastal zone) is located much above the theoretical line. The enrichment of this point in sulphates is probably related to agricultural pollution (this point also registered a high nitrate content). Figure 4b shows the sodium vs chloride graph. Most of the points are situated below the theoretical line. Given that Na should balance the chloride content, there should be a cation-exchange process which reduces the Na content. Na is taken up by the exchanger and Ca is released. This process is evident at point 20, which presents a notable excess of Ca (Figure 4c).

The Ca vs chloride graph (Figure 4c) shows an enrichment in Ca at those points situated above the theoretical line, with two points (7 and 20) showing an extremely high Ca content in relation to the others. This enrichment may be due to dissolution of calcite and/or Na-Ca exchange. The Mg vs chloride graph (Figure 4d) indicates an excess of Mg in certain waters. This excess may be linked to dissolution of the dolomite and/or the flushing of marine formations.

A plot of Ca vs bicarbonate may serve to characterize the dissolution phenomenon. This graph (Figure 5a) provides good alignment between most of the points following the 1:1 dissolution line of the carbonates. An exception is found in the waters of points 7 and 20 which, as indicated above, are enriched in Ca by exchange with Na. The Mg vs bicarbonate graph (Figure 5b) reveals that most of

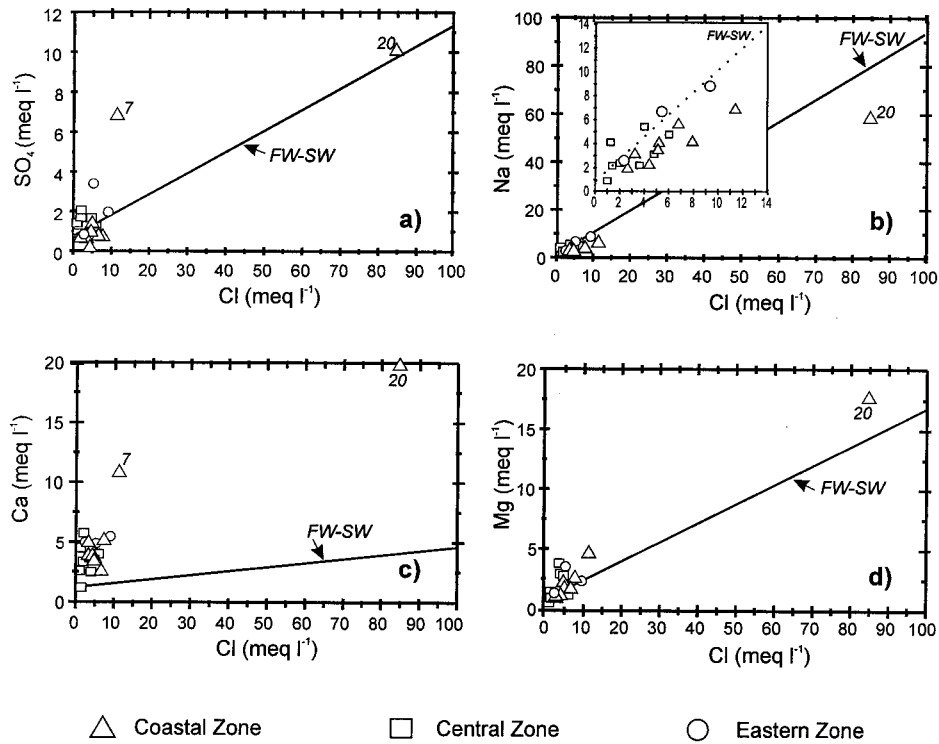


Figure 4. Relationship between chloride (meq l^{-1}) and a) sulphate; b) Na; c) Ca; d) Mg; FW-SW: theoretical mixing line between freshwater and seawater. In twenty-one water samples from the Temara aquifer (October 1994).

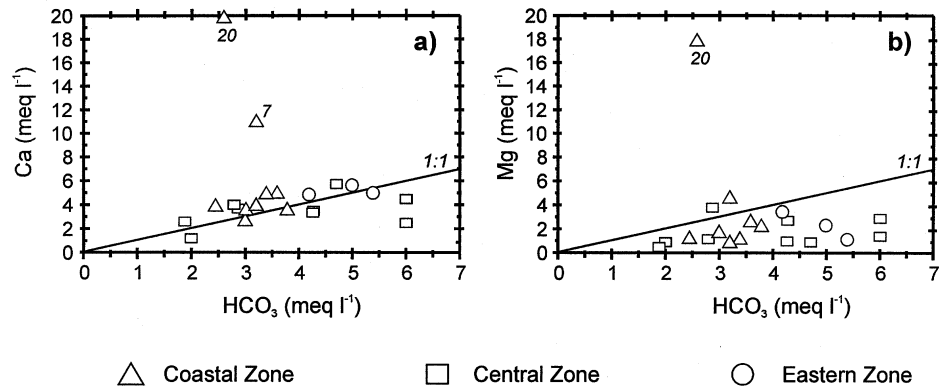


Figure 5. Relationship between a) Ca vs bicarbonate; b) Mg vs bicarbonate (meq l^{-1}). In twenty-one water samples from the Temara aquifer (October 1994).

the points are displaced below the 1:1 dissolution line of the bicarbonates. Custodio (1987) showed that the Sr content was between 0.2 and 1 mg l⁻¹ in freshwater – but in some instances attained higher values – and between 8 and 13 mg l⁻¹ in seawater. Turekian (1978) indicated that the concentration of Sr in seawater was 7.65 mg l⁻¹, though in our case it was found to be 6 mg l⁻¹. The Sr enrichment of groundwaters in contact with the carbonate rocks can be attributed to the release of Sr during the recrystallization of aragonite into calcite (Gimenez, 1994), given that the proportion of Sr in aragonite present is likely to be greater than that of calcite. After several phases of dissolution-precipitation of carbonate rocks, Sr concentration increases in the water (Tulipano and Fidelibus, 1991).

A plot of Ca, Mg and Sr concentration at the twenty-one points in the current study (Figure 6) shows that these ions tend to vary together. However, the magnitude of the variations of these ions is different with distance from the coast. This shows that the presence of Sr in the aquifer is linked to the dissolution of carbonate rocks. However the high values of point 20 indicates that mixing of fresh and seawater occurs around this point.

3.4. RESIDENCE TIME

The values of the Maturity Index were low, varying between 0 and 0.0038 (Table III). These values indicate that the aquifer waters have undergone recent infiltration, and that the increased salinity at certain points in the southwestern coastal zone are not linked to the existence of fossil waters in the aquifer, but rather to the flushing by infiltration water of the marine formations which still retain salts (points 2 and 9). The Maturity Index obtained for point 20 is not significant since it is determined by the mixing of seawater with the aquifer water. Figure 6 also reflects a parallel evolution of Sr and MI.

3.5. EQUILIBRIUM STATES OF THE WATER

It is apparent that Cl content increases in the flow direction (Cl/HCO₃) as do the TDS (Total Dissolved Solids, Table IV). It is also evident that the dissolution potential is greater for dolomite and proves to be of the same order of magnitude for calcite and aragonite. The low value of P_{CO2} is notable at point 14 (Table IV), corresponding to the less aggressive water. By contrast, point 5 shows much higher values being located in the zone where, according to the stratigraphic column obtained in this sector, the mixing of waters from the deep and upper aquifers occurs. The values of the saturation index of aragonite, calcite and dolomite are less than zero, substantiating the existence of dissolution phenomenon which, from one part of the karstification phenomenon to the other, contribute to the enrichment of the aquifer waters in Ca, Mg and bicarbonate.

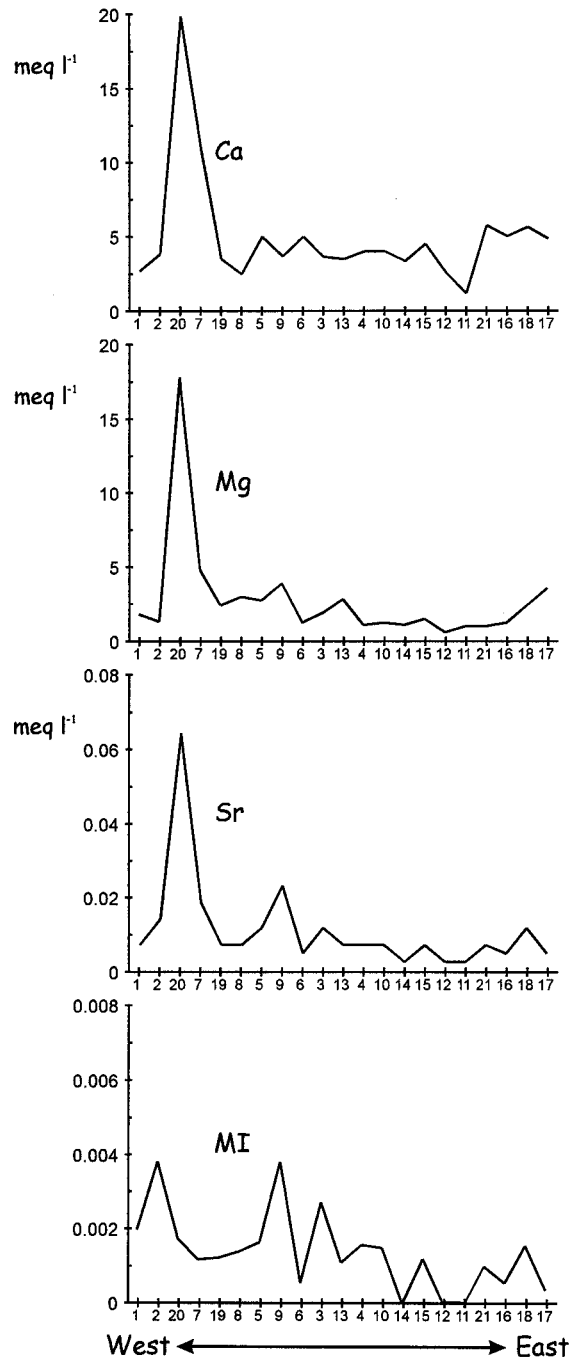


Figure 6. Evolution of the contents (meq l^{-1}) in Ca, Mg, Sr and the Maturity Index (MI) from west to east. In twenty-one water samples from the Temara aquifer (October 1994).

TABLE III

Maturity Index (MI= $\Delta\text{Sr}/\Delta(\text{Ca}+\text{Mg})$). Point 11 was chosen as the reference sample. Ca, Mg, Sr in meq l⁻¹. In water samples spread over the Temara aquifer (October 1994)

N°	Ca	Mg	Sr	Ca+Mg	$\Delta(\text{Ca}+\text{Mg})$	ΔSr	Mi
1	2.69	1.71	0.007	4.40	2.31	0.0046	0.0020
2	3.84	1.23	0.014	5.07	2.98	0.0114	0.0038
3	3.64	1.80	0.011	5.44	3.35	0.0091	0.0027
4	4.00	0.98	0.007	4.98	2.89	0.0046	0.0016
5	5.00	2.63	0.011	7.63	5.54	0.0091	0.0016
6	5.00	1.15	0.005	6.15	4.06	0.0023	0.0006
7	10.97	4.68	0.018	15.65	13.56	0.0160	0.0012
8	2.49	2.87	0.007	5.36	3.27	0.0046	0.0014
9	3.68	3.78	0.023	7.46	5.37	0.0205	0.0038
10	4.00	1.15	0.007	5.15	3.06	0.0046	0.0015
11	1.19	0.90	0.002	2.09	****	****	****
12	2.59	0.49	0.002	3.08	0.99	0.0000	0.0000
13	3.49	2.71	0.007	6.20	4.11	0.0046	0.0011
14	3.34	0.98	0.002	4.32	2.23	0.0000	0.0000
15	4.49	1.39	0.007	5.88	3.79	0.0046	0.0012
16	5.00	1.15	0.005	6.15	4.06	0.0023	0.0006
17	4.84	3.45	0.005	8.29	6.20	0.0023	0.0004
18	5.63	2.30	0.011	7.93	5.84	0.0091	0.0016
19	3.49	2.30	0.007	5.79	3.70	0.0046	0.0012
20	19.86	17.68	0.064	37.54	35.45	0.0616	0.0017
21	5.73	0.90	0.007	6.63	4.54	0.0046	0.0010

TABLE IV

Total Dissolved Solids (mg l⁻¹. TDS = $\Sigma\text{ions} - 1/2 \text{HCO}_3$), Cl/HCO₃, PCO₂, and saturation indices of aragonite, calcite and dolomite in water samples spread over the Temara aquifer (October 1994)

N°	TDS (mg l ⁻¹)	Cl/HCO ₃	PCO ₂ (atm × 10 ⁻³)	ISarag	IScal	ISdol
14	577	0.48	3.39	-0.550	-0.404	-1.360
8	770	0.67	9.13	-0.196	-0.050	-0.057
5	810	2.20	14.6	-0.598	-0.451	-1.101
7	1507	3.58	10.3	-0.082	-0.065	-0.144
20	5684	32.71	16.4	-0.508	-0.361	-0.672

4. Conclusions

The waters of the upper aquifer (Quaternary calcarenites and sandstones) are in general of good chemical quality according to Moroccan Drinking Water Standards, following the norms of the World Health Organization, and are characteristic of the central zone. These waters are calcium-bicarbonate type. Their enrichment with bicarbonate, Ca and Mg in the central zone arises from the dissolution of carbonate rocks under the influence of increased P_{CO_2} in the groundwater – somewhat higher P_{CO_2} values were obtained in the same area –, probably due to the degradation of agricultural organic matter, among other factors.

The waters of the southwestern coastal zone are characterized by high salinity compared with those of the central sector. The lack of recharge, coupled with excess pumping, has lowered the piezometric level and has thereby provoked seawater intrusion (point 20). The Miocene marls in the coastal sector are not thick. Thus, the waters of the upper aquifer, low in salinity, mix with those of the lower aquifer which have higher salinity. The facies of the waters in this sector is sodium chloride. The enrichment of the waters in chloride and sodium results from the flushing of the marine formations (Miocene marls) which constitute the top of the lower aquifer and which still contain the salts. The high salinity registered at point 7 may originate from a combination of several factors: washing from marine formations, dissolution of the carbonate rocks and agricultural pollution. Point 7 showed high nitrate contents (2.12 meq l^{-1}), chloride (11.41 meq l^{-1}), and sulphate (6.97 meq l^{-1}), which coincide with the principal components of the fertilizer used by farmers in the area. The enrichment of this point in Ca may be related to the dissolution of calcite and a Na-Ca exchange. The exceptional salinity of point 20 may originate, apart from the combined factors cited above for point 7, from seawater intrusion.

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