

Understanding the origin of salinization of the Plio-quaternary eastern coastal aquifer of Cap Bon (Tunisia) using geochemical and isotope investigations

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Abstract As in many other semi-arid regions, the Plio-quaternary aquifer of the eastern coast of Cap Bon peninsula (NE Tunisia) shows a parallel increase in over-exploitation and mineralization of groundwater resources and so the water quality is deteriorating. Different methods using geochemistry (ions Na^+ , Cl^- , Ca^{2+} , Mg^{2+} , Br^-) and stable isotopes (^{18}O , ^2H) are compared with the hydrodynamic information for identifying the main processes involved in the increase of salinization. Along the coast, intrusion of seawater resulting from groundwater overexploitation is identified, but is not the only cause of qualitative degradation: the development of irrigation that induces soil leaching and transfer of fertilizers to groundwater over the whole aquifer extent is another major reason for the increase in salinization. A total of 48 groundwater wells were sampled to obtain additional information on the hydrochemical characteristics of the groundwater defined in previous studies.

Keywords Hydrogeology · Geochemistry · Isotopes · Coastal aquifer · Tunisia

Introduction

In semi-arid coastal zones, freshwater resources are often threatened by the intrusion of seawater into the aquifer systems. However, the high salinity encountered can also have other origins, natural or anthropic, such as dissolution of halite and gypsum, concentration by evaporation, downward leakage from the unsaturated zone and pollution (Custodio and Bruggeman 1987; Jones et al. 1999; Ghabayen et al. 2006; Trabelsi et al. 2007; Bouchaou et al. 2008; Marandi and Karro 2008). The distinction between the different mechanisms of salinization permits us to reconstitute the origin of groundwater, their progress and to imagine their future evolutions. Among the geochemical criteria that can help to identify seawater intrusion as opposed to other sources of salinity in coastal zones, various ionic ratios can be used such as Na/Cl , Br/Cl , Ca/Mg , $\text{Ca}/(\text{HCO}_3 + \text{SO}_4)$, as well as the isotopes of ^{18}O and ^2H , ^{34}S and ^{11}B (Yurtsever 1994; Jones et al. 1999). Cl and Br are ubiquitous solutes in groundwater. As several processes change Br/Cl ratios in a predictable manner, they are invaluable tracers of groundwater processes (Cartwright and Weaver 2005). Stable isotopes of oxygen-18 and deuterium are commonly used in regional groundwater studies to identify flow regimes and sources of recharge (Clark and Fritz 1997). They are generally considered to be transported conservatively in shallow aquifer settings (Vitvar et al. 2005). Variations in the stable isotope composition of components in catchment water are caused by: natural variations in the isotopic composition of rainfall (Mook 2001), mixing with different waters (Leduc et al.

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2007) and evaporation (Gonfiantini 1998). In the case where no significant evaporation of rainwater occurs before and after infiltration, the groundwater oxygen and hydrogen isotopes data can provide important information on the salinization processes in coastal aquifers. Like Br, stable isotopes can be therefore used in conjunction with Cl to constrain the origin and proportion of mixing between fresh and saline water.

The Tunisian shoreline extends for 1,300 km, with the coastal zone width ranging from 20 to 60 km and a total area of approximately 40,000 km² (Gaaloul and Cheng 2003). The dry climate conditions in this zone and the heavily irrigated agriculture have led to intensive groundwater exploitation. Consequently, the coastal aquifers are at great risk of saltwater intrusion. The Plio-quadernary aquifer of the eastern coast of Cap Bon, in northeastern Tunisia, is typical of a situation seen all around the Mediterranean basin. The natural balance of groundwater, highly dependent on the great climate variability, has been completely disrupted for several decades by an extreme increase in irrigation that affects the intensity, distribution and quality of incoming and outgoing flows. Gaaloul and Cheng (2003) explained the hydrogeological and hydrochemical evolution of coastal aquifers in Tunisia by anthropogenic activities. Various salinization processes were examined and identified in the groundwater of the Santo Domingo irrigation district in Baja California Sur, Mexico (Cardona et al. 2004).

Previous studies, such as that in 2001 (Paniconi et al. 2001) covering the southern part of the aquifer, have explained water mineralization by the process of mixing with seawater without any other source of salinity. This phenomenon exists, but is probably not the sole factor responsible for mineralization. Therefore, it is better to try to determine the origin of this mineralization. To do this, geochemical information will be used and the results compared with the hydrodynamic data.

The purpose of this study was to determine the origin of this salinization by exploiting the geochemical information and to compare the results with the hydrodynamic data of the coastal area in the Plio-quadernary aquifer of the eastern coast of Cap Bon, Tunisia. This was achieved by using chemical inorganic indicators as major, minor and stable isotopes.

Main features of the study area

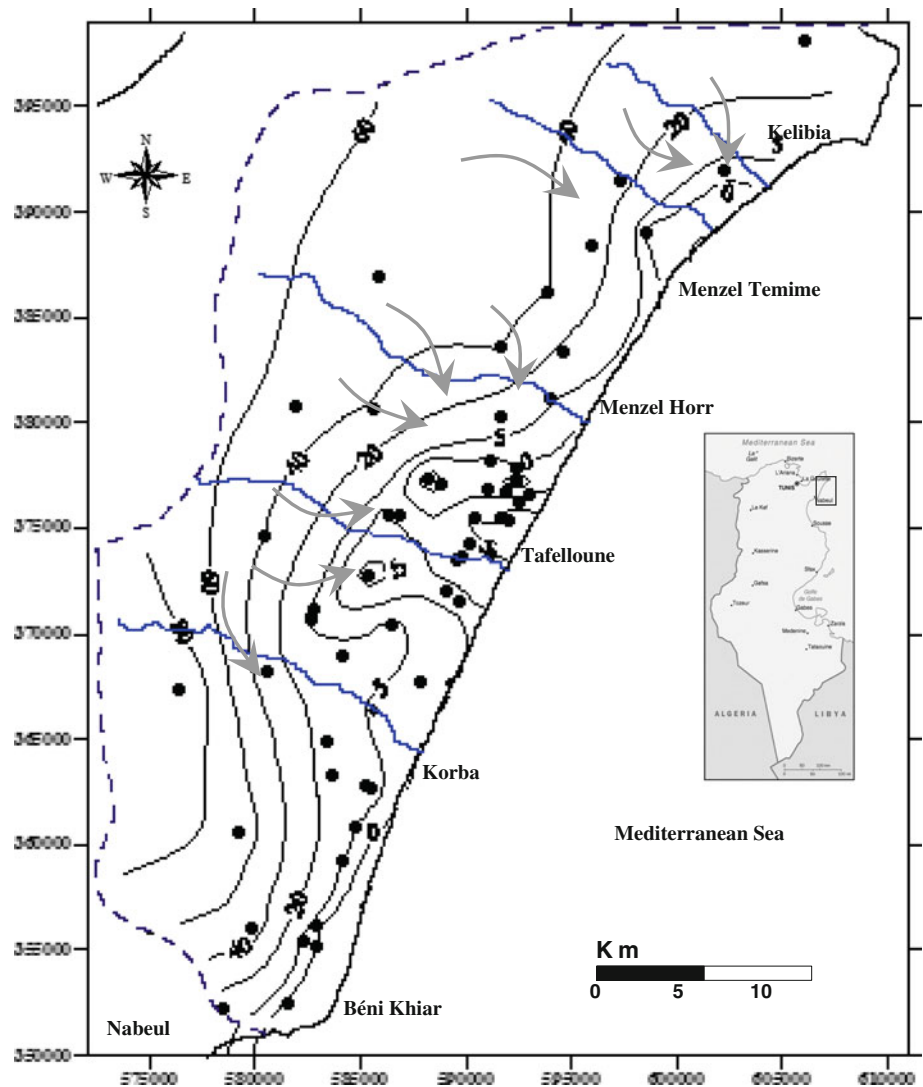
The Cap Bon peninsula is located in northeastern Tunisia and is mainly cut off, being surrounded by the sea on three sides (Fig. 1). The plain of the east coast extends 45 km in length from Béni Khiar to Kélibia and about 17 km in width from the sea to the foot of the Djebel Abderrahmane

mountain range (637 m). The landscape is a coastal plain slightly sloping (3%) toward the sea. The plains, low and flat, are lined by a sandy coastline, which separates a string of salt lakes (sebkhas) from the sea. This region is an important touristic, industrial and, above all, agricultural area, with a population approaching 100,000, concentrated along the coast around the towns. The Mediterranean climate is subhumid to semi-arid. The average annual temperature varies from 17 to 19°C. The wettest months are November–March, and the driest are July and August. The average annual rainfall is 450–500 mm, but varies greatly: in Korba, the extremes observed between 1960 and 2004 were 159 and 821 mm, in 1968 and 2004, respectively. Potential evapotranspiration, calculated using the Riou method (Riou 1980), exceeds 1,100 mm/year.

The plain is composed of three aquifers: a groundwater aquifer in the sandy Plio-quadernary formations, which covers 475 km² and the thickness of which varies from 30 to 150 m, and two deeper aquifers in the Miocene and Oligocene sand and sandstone (Fig. 2). The Plio-quadernary, Miocene and Oligocene aquifers have the same borders to the east and south, whereas in the north and west, the Miocene and Oligocene aquifers go beyond that of the Plio-quadernary for more than 300 km². The Oligocene is tapped at the foot of the Abderrahmane mountain anticline, west of the study area. The Miocene is tapped in the south. These two aquifers plunge quickly, sometimes more than 1,500 m deep in the plain, by a series of sheets of faults active during the Neogene. The Miocene aquifer is separated from the Plio-quadernary by a thick layer of clay of approximately 20 m, which is sufficiently impermeable and continuous to allow a hydraulic head for deep aquifers. The shallow groundwater aquifer has a flow direction from inland Cap Bon toward the coast (W–E or NW–SE) (Fig. 1). The average hydraulic gradient was 4.5 ‰ in 1980 when the aquifer was still in its natural condition. In the Miocene aquifer, water also flows from the anticlinal border to the west toward the sea. The piezometry of the two deep aquifers is higher everywhere than that of the shallow groundwater aquifer, and the average difference in hydraulic head is about 10 m.

On the east coast, the use of water resources has almost doubled in the last decades (Jemai 1998). Long periods of draught and excessive pumping have greatly disturbed the balance of the shallow groundwater aquifer and furthered seawater intrusion. The Plio-quadernary aquifer is most in demand for agricultural and domestic needs. The collection of water comes from an increasing number of shallow wells (just an open hole in the ground) ranging in depth from 15 to 50 m. Official annual figures indicate water retrieval of 54 E–6 m³ for an interannual average groundwater recharge estimated at 50 E–6 m³ (DGRE 2004).

Fig. 1 Location of sampled points of 2001 and piezometric contour map (in meters above mean sea level) of the eastern coast aquifer of Cap Bon



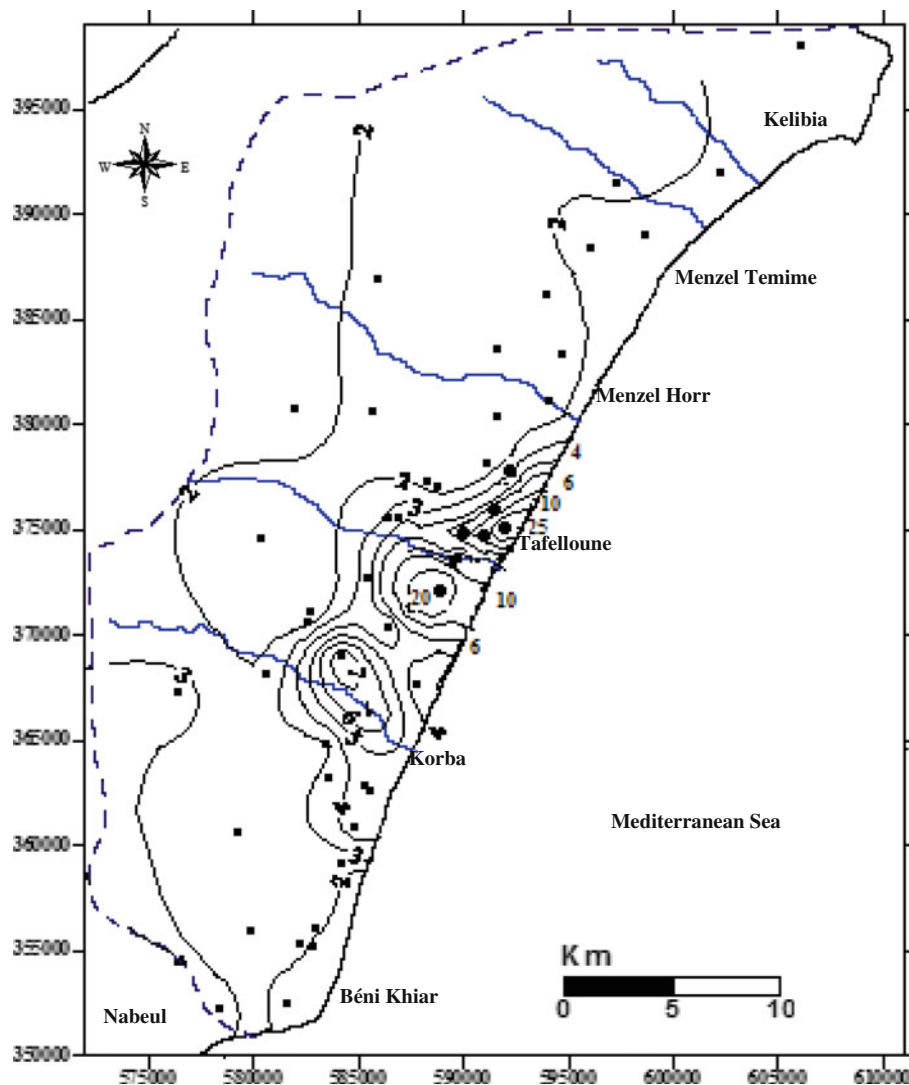
Effective infiltration (rainfall minus evaporation and surface runoff) is estimated to be <7% of annual precipitation and as low as 5%. It is interesting to note that, based on these estimates and using 22 mm as effective annual infiltration, the volume of water recharged to the aquifer from a combination of rainfall and irrigation is approximately $18 \text{ E}-6 \text{ m}^3$ annually; comparing this value with the $54 \text{ E}-6 \text{ m}^3$ estimated annual pumping rate gives an idea of the degree of overexploitation of the aquifer.

This has caused the emergence of piezometric depression cones in various places in the water table, up to -12 m below msl in the regions of Korba and Tafelloune (Fig. 1) and the abandonment of approximately one-third of 9,240 surface wells of the Plio-quaternary aquifer (Jemai 1998; DGRE 2004). The lowest piezometric decline is 12 m between 1972 and 2001 in Tafelloune. On the other hand, the deep aquifer shows no recent piezometric depression caused by pumping.

Methodology and analytical data

Previous chemical data come from work undertaken in 1962, 1974, 1987, 1988 and 1997, often in poorly defined conditions. For this study, geographical position, depth to water table, electric conductivity, pH and temperature were measured in 48 water samples from the Plio-quaternary aquifer, dug wells, boreholes, and piezometers in 2001, 2002 and 2003 (Figs. 1, 3). Samples were also collected for identification of major elements and isotopes ^2H and ^{18}O . Samples were taken after purging some piezometers. Boreholes and dug wells did not need to be purged, because at the time of sampling water was extracted from these wells. Table 1 provides the main results from the spring of 2001 (end of the rainy period and beginning of heavy agricultural pumping) as well as the Br- and Cl contents in 2003. Twelve additional samples helped to characterize the deep aquifers.

Fig. 2 Groundwater salinity map measured as TDS (g/l) in 2001



Chemical analysis of the water samples was performed at the National Centre for Nuclear Science and Technologies, Isotope Hydrology Laboratory, (Sidi Thabet, Tunisia). Major cation (Ca, Mg, Na, and K) concentrations were analyzed in filtered samples using an Analytic Jena atomic absorption spectrometer with a furnace AAS Vario 6 and anion (Cl, SO₄ and NO₃) concentrations were analyzed in filtered samples using a Dionex DX 120 ion chromatograph equipped with an AG14 and an AS14 Ion Pac columns and an AS-40 auto-sampler. Bromide concentrations were analyzed using a Dionex DX 120 ion chromatography equipped with an AG14 and an AS14 Ion Pac columns at the Avignon University, France. The charge balance between major anions and cations was better than $\pm 5\%$.

Isotope analyses of the water samples (²H and ¹⁸O) were performed at the Institute of Groundwater Ecology-GSF Research Centre (Neuherberg/Germany) and supported by IAEA through TC project TUN/8/015 and TUN/8/017. Stable isotopes of oxygen and hydrogen were determined

by isotope ratio mass spectrometry in a Finnigan MAT Gas Bench and analyzed using continuous flow on a Finnigan MAT 252 mass spectrometer. The $\delta^{18}\text{O}$ values in samples were analyzed via equilibration with CO₂ at 25°C for 24 h (Epstein and Mayeda 1953) and for the $\delta^2\text{H}$ values via reaction with Cr at 850°C (Coleman et al. 1982). Both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were determined relative to internal standards that were calibrated using IAEA SMOW standards. Data were normalized following Coplen (1988) and are expressed relative to V-SMOW. Samples were measured at least in duplicate and the precision of the analytical measures as $\pm 0.1\%$ for $\delta^{18}\text{O}$ and $\pm 1\%$ for $\delta^2\text{H}$. The results of this study were compared with previous information.

Preliminary interpretations

The salinity (total suspended solid contents) of the Plio-quaternary aquifer is very heterogeneous, varying between

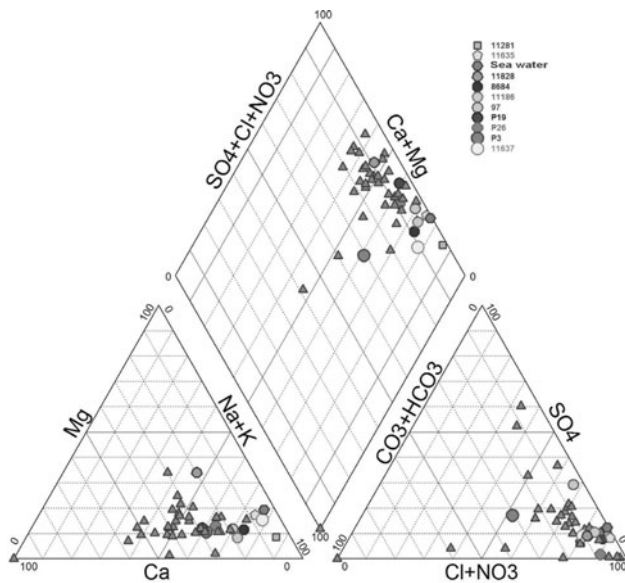


Fig. 3 Piper diagram showing the composition of the Plio-quaternary groundwater of the eastern coast aquifer of Cap Bon in 2001

0.8 and 36.3 g/l (median 2.3 g/l). There is no link between mineralization and depth of water: the deepest water is not the saltiest. The dominant chemical feature is sodium chloride. The samples from the Miocene have mineralization varying between 0.6 and 1.4 g/l (median 0.8), with chemical features identical to that of the Plio-quaternary water.

In 1963, well before the present overexploitation, salinity of the Plio-quaternary water was characterized by values ranging from 0.6 to 8.7 g/l (median of 1.9 g/l calculated at 101 water points, most between 0.9 and 3 g/l). The upstream part was more mineralized than the coastal area, which was almost always <2 g/l. The current upstream salinity has not changed significantly but it has now reached extreme values of 20–30 g/l near Korba and Tafelloune.

The impact of this increase in salinity is felt more and more as the number of abandoned wells keeps increasing. Agriculture output is impacted on and damage to topsoil may have taken place. The risk of wells being contaminated increased significantly between 1963 and 2001. Indeed, 95% of the wells sampled in 1963 presented a low risk for use in irrigation; in 2001 this number dropped to 65%. Wells presenting a high risk practically did not exist in 1963; currently, water from approximately 11% of the sampled wells presents such a high risk for use in irrigation. Several hydrochemical investigations (classification of MOOR, BREUCK and STUYEZAND) have been conducted (Jemai 1998) and they confirm that the aquifer is prone to high risks of salinization.

At the southern end of the plain, the salinity of the Plio-quaternary has remained low (0.65 g/l). These contrasting

developments are probably the combined result of many phenomena.

The increase in salinity seems to be linked to hydrodynamic degradation as suggested by similarities in piezometry and salinity maps, especially in the Tafelloune region (Fig. 3). Piezometric depression extended toward the interior of the country and was augmented: about 20 km² in 1970, 30 km² in 1988 and 50 km² in 2001 (Fig. 1), and mineralization increased as well. A seawater intrusion is therefore a very plausible hypothesis for the increase in mineralization, but not necessarily the only one.

The increase of mineralization confirms the insufficiency or lack of drainage from the Miocene, the mineralization of which is for 90% of the measures <1 g/l, including in the piezometric depression area. The explanation for this increase in the Plio-quaternary aquifer must therefore be searched for in this aquifer and not in the Miocene.

Irrigation water return flow into the aquifer is also a plausible hypothesis. Large-scale irrigation has greatly developed since the 1980s and affects the entire aquifer. The thickness of the unsaturated zone varies from 1 to 31 m throughout the aquifer (and from 12 to 28 m in the current piezometric depression). Nitrate content can be considered to represent agricultural pollution: the median of analyses from 2001 (90 mg/l) is sufficient to show the magnitude of the problem. The absence of correlation between nitrate and thickness of the unsaturated zone indicates that all the area may be contaminated by this pollution.

The chemical composition of shallow groundwater from Plio-quaternary plotted in a piper diagram (Fig. 3) shows a trend of water classified under a sodium chloride type and sulfated calcic and magnesium type. Figure 3 shows also salt water represented by reference seawater sample collected near the studied area. The piper diagram also shows that water in the wells that underwent a seawater intrusion shows Na–Cl trend actually near the coast and is characteristic of seawater (located in the region of the piezometric depression), the composition depending on the mixing ratios. The samples taken at the other points located far from the coast have a chlorinated and sulfated chemical trend and are thus excluded from any contamination by seawater.

Specific interpretations

- *The Na⁺/Cl⁻ relationship* Chloride is very strongly correlated with sodium in the majority of samples (Fig. 4). The predominance of sodium and chloride is explained by the proximity of the sea, via the spray and/or a progress of seawater intrusion. Even for those

Table 1 Sampling sites, chemical and isotopic composition of the analyzed groundwater samples

No BIRH	PL (m)	Lat. LAMBERT	Long. LAMBERT	Cond (ms cm ⁻¹)	R.S	Ca	Mg	Na	K (mg l ⁻¹)	SO ₄	Cl	HCO ₃	NO ₃	¹⁸ O ‰	² H ‰	Cl 2003	Br 2003
P1	33.0	606050	398100	3.4	2144	272.5	53.5	379.3	27.4	269.0	709.1	219.6	66.3	-4.84	-28.0	923	2.36
P3	1.2	602200	391950	3.2	2035	168.4	38.9	418.4	1.8	268.9	581.4	610.1	30.4	-1.95	-11.8	511.2	1.62
P19	3.5	589550	373500	5.5	3520	300.6	77.8	705.8	11.7	182.5	1446.5	122.0	30.4	-3.55	-22.6	2612.8	9.3
P26	8.3	584150	369000	13.1	8371	537.1	179.9	1572.5	132.9	96.1	3828.0	610.1	3.1	-1.56	-9.5	3507.4	10.76
97	3.7	585600	366350	11.4	7296	460.9	179.9	1986.3	25.0	1690.6	2765.3	280.6	191.1	-4.46	-27.1	1775	6.52
892	-7.7	585400	372750	5.4	3469	380.8	121.6	611.5	13.3	278.6	1538.7	122.0	226.2	-4.39	-26.9	1008.2	4.2
996	13.6	583400	364850	4.1	2650	228.5	58.3	558.7	3.9	216.1	1049.4	207.4	105.3	-4.90	-28.6	1079.2	4.27
1129	27.3	580600	368250	3.2	2067	148.3	41.3	478.2	11.7	144.1	794.1	244.0	22.6	-5.05	-29.1	852	3.42
3093	40.9	591600	383575	2.0	1265	200.4	29.2	151.7	19.2	172.9	304.9	231.8	145.1	-4.70	-27.5	284	1.18
3113	5.6	594025	381175	1.8	1153	144.3	2.4	165.5	46.9	115.3	297.8	219.6	46.8	-5.31	-30.8	213	0.69
3190	52.9	581900	380800	3.8	2451	240.0	46.0	494.3	1.0	360.2	907.6	231.8	7.8	-4.71	-28.4	962.05	
3202	47.0	585850	386950	3.0	1920	192.4	85.1	409.2	4.7	768.0	389.0	219.0	3.0	-1.66	-11.8	255.6	0.91
4814	101.5	576400	367350	5.3	3417	260.5	70.5	806.9	7.0	499.5	1127.4	268.4	105.3	-4.48	-25.6	866.2	2.84
5610	-1.6	581600	352500	2.0	1293	148.3	48.6	190.8	43.0	312.2	326.2	213.5	37.1	-3.78	-22.3	347.9	0.65
5729	10.9	591650	380350	2.4	1510	168.3	116.7	232.2	3.1	144.1	546.0	170.8	35.5	-2.03	-11.2		
5743	28.8	596000	388400	3.8	2400	172.3	75.4	549.5	5.5	240.1	801.2	219.6	218.4	-4.42	-24.8	745.5	
5972	40.2	593900	386250	2.3	1485	232.5	17.0	151.7	27.4	115.3	390.0	170.8	167.7	-4.55	-26.0	411.8	1.51
5994	25.8	597300	391550	2.9	1862	208.4	31.6	338.0	5.1	244.9	567.2	134.2	105.3	-2.55	-13.8	610.6	
6077	15.6	594650	383375	2.5	1613	220.4	29.2	239.1	0.0	172.9	439.6	183.0	132.6	-3.00	-17.6	454.4	
6686	38.1	585650	380600	2.7	1702	212.4	29.2	278.2	2.7	168.1	496.3	244.0	140.4	-4.77	-27.1	497	
8088	50.4	579850	356000	3.1	1958	240.5	31.6	338.0	5.9	230.5	638.2	183.0	187.2	-4.68	-27.6	596.4	
8315	4.8	584800	360850	7.4	4762	320.6	158.0	1128.8	50.8	345.8	1879.0	256.2	159.9	-4.65	-27.3	1846	5.87
8346	0.4	582950	356150	3.6	2323	216	98.4	414	15.6	288	816.5	207.4	241.8	-5.14	-30.3	1178.6	
8377	72.4	579200	360650	3.1	2010	212.4	38.9	273.6	23.5	240.1	460.9	256.2	341	-4.95	-28.4	553.8	
8400	4.7	584150	359200	3.1	1971	176.4	43.8	393.1	19.6	134.5	687.8	231.8	128.7	-5.04	-28.5	1079.2	4.01
8403	10.4	578400	352250	5.7	3648	440.9	109.4	659.8	23.5	1090.2	1191.2	207.4	124.8	-4.28	-25.8	440.2	1.69
8420	-0.4	589700	371550	3.8	2413	204.4	46.2	496.6	3.9	201.7	943.0	146.4	93.6	-4.50	-26.0	653.2	2.33
8647	2.0	582600	370700	2.7	1696	228.5	43.8	200.0	13.7	1690.6	638.2	231.8	89.7	-5.15	-29.9	752.6	11.92
8684	4.0	587800	367700	5.1	3232	144.3	68.1	811.5	43.0	206.5	1361.4	256.2	63.6	-2.46	-13.4	2428.2	11.16
8737	0.8	592350	377800	5.6	3578	360.7	102.1	682.8	9.4	201.7	1666.3	195.2	111.9	-4.42	-25.7	1902.8	9.36
8774	1.6	582250	355400	4.7	2995	288.6	141.0	466.7	8.2	139.3	1205.4	341.6	110.8	-4.76	-28.2	1164.4	3.59
8820	40.6	580400	374600	2.3	1453	96.2	34.0	383.9	14.5	172.9	304.9	231.8	145.1	-5.05	-28.3	568	1.78
8894	-2.8	586350	375650	4.5	2848	340.7	65.6	418.4	64.9	134.5	1120.3	329.4	163.8	-4.60	-26.6		
10959	-2.0	591000	376850	1.8	1162	40.1	31.6	273.6	14.1	5.8	581.4	61.0	2.0	-4.44	-26.6	596.4	
10995	-0.2	591950	376750	5.0	3226	280.6	12.2	740.3	18.4	5.3	1616.7	61.0	2.3	-4.02	-23.4		

Table 1 continued

No	PL (m)	Lat. LAMBERT	Long. LAMBERT	Cond (ms cm ⁻¹)	R.S	Ca	Mg	Na	K (mg l ⁻¹)	SO ₄	Cl	HCO ₃	NO ₃	¹⁸ O δ‰	² H δ‰	Cl 2003	Br 2003
10996	1.6	582850	355200	1.6	1023	144.3	15.8	121.8	7.4	48.0	361.6	97.6	12.9	-5.33	-30.8	340.8	1
11186	3.7	590150	374300	5.9	3802	188.4	51.1	823.0	52.4	240.1	1382.7	170.8	82.3	-4.55	-26.4	13035.6	43.21
11191	6.4	590450	375500	3.7	2355	156.3	70.5	501.2	12.5	11.5	1205.4	61.0	4.3	-4.35	-27.0	3024.6	13.85
11635	0.4	592500	376250	38.8	27160	681.4	923.8	7402.8	211.1	1729.0	13862.1	378.2	13.7	-2.26	-15.6		
11637	0.8	593000	376550	14.9	10430	200.4	289.3	2699.0	139.2	696.4	4608.9	1037.1	2.3	-4.36	-25.4		
11650	4.3	591100	373800	3.3	2331	200.4	24.3	494.3	10.9	149.8	822.5	292.8	43.3	-4.65	-26.3		
11829	6.8	586450	370450	3.8	2432	268.5	80.2	434.5	10.9	105.7	1063.6	305.0	53.0	-4.33	-24.7	994	3.53
11269	-8.7	588200	377350	2.7	1702	184.4	60.8	262.1	11.7	3.4	595.6	317.2	107.7	-4.47	-27.1	745.5	
11281	1.0	591650	375500	36.9	36315	420.8	437.2	8196.4	190.4	1916.4	13009.2	408.8	14.9	-3.22	-20.1		
11828	4.3	586900	375650	6.4	4090	250.5	263.8	666.7	18.8	278.6	1765.6	353.8	156.0	-4.48	-27.8	1803.4	6.83
11869	3.2	582750	371150	1.3	858	84.2	26.7	158.6	4.7	25.9	248.2	317.2	17.9	-4.80	-28.9	284	
13143	-1.05	589000	372000	30.8	21050	800	720	5083	77	1919.2	13824	414.8	57.3				
13207	-0.66	589800	373600	14.9	9960	700	480	2355	43	905.2	5614	262.3	188.1				

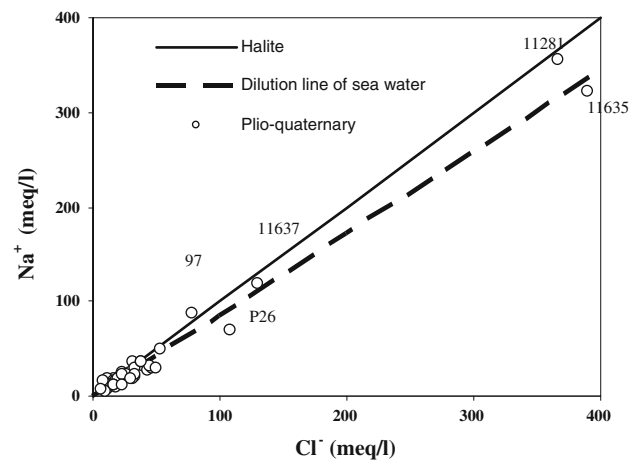


Fig. 4 [Na⁺]/[Cl⁻] correlation in groundwater of the eastern coast aquifer of Cap Bon

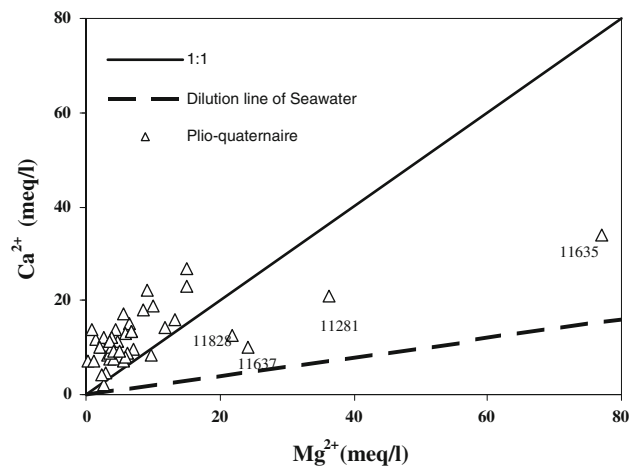


Fig. 5 [Ca²⁺]/[Mg²⁺] correlation in the groundwater of the eastern coast aquifer of Cap Bon

taken far from the sea, the molar relationship Na⁺/Cl⁻ does not differ very significantly from that of the Mediterranean (0.86) (Jones et al. 1999; Fedrigoni et al. 2001; Lee and Song 2007; Abou Zakhem and Hafez 2007) and therefore is insufficient in distinguishing the origin of the water.

- *The Ca²⁺/Mg²⁺ relationship* Groundwater is characterized by a great variability in Ca²⁺ and Mg²⁺ contents, but most cases show a predominance of Ca²⁺ compared to Mg²⁺ (Fig. 5). The samples 11635, 11634, 11281 and 11828 are the only ones to have a Ca²⁺/Mg²⁺ ratio <1, which might indicate a mixture with seawater (marine ratio = 0.2) (Vengosh and Ben-Zvi 1994). Moreover, they are situated in the area where salinity is the most elevated.
- *The Br⁻/Cl⁻ relationship* The Br⁻/Cl⁻ relationship helps identify the possibility of seawater intrusion (Fedrigoni et al. 2001; Takrouni 2003; Kim et al. 2003),

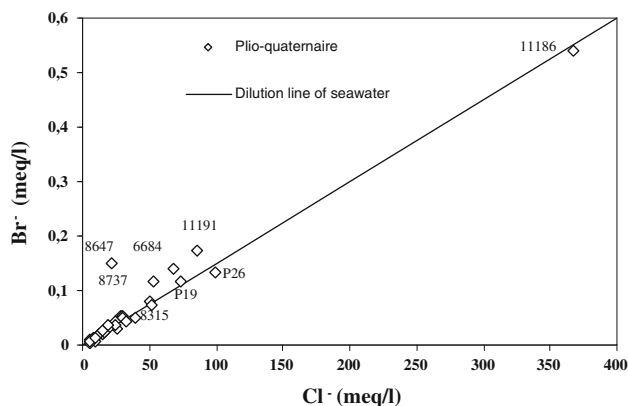


Fig. 6 Content of Br^- and Cl^- in the groundwater of the eastern coast aquifer of Cap Bon

since it is relatively constant (1.5×10^{-3}) in the sea considering the extremely long residence time in the oceanic masses. In the Plio-quadernary aquifer, the Br^-/Cl^- relationship is not distinctive (Fig. 6): more than two-thirds of the points are within a range of 20% from the sea relationship. This proximity can be explained both by continental waters mixing with seawater, and also by an influence of salt spray on the infiltrated rainwater.

- **Stable isotopes** The deuterium–oxygen 18 diagram shows three groups (Fig. 7). In the first ($\delta^{18}\text{O}$ between -5.5 and -4.3 ‰ V-SMOW), points are located between the global meteoric water line (GMWL) and the local meteoric water line of Tunis-Carthage station, the equation for which is as follows: $\delta^2\text{H} = 8\delta^{18}\text{O} + 12.4$ (Celle-Jeanton et al. 2001). The hypothesis of an important contribution of the current rains to the recharge

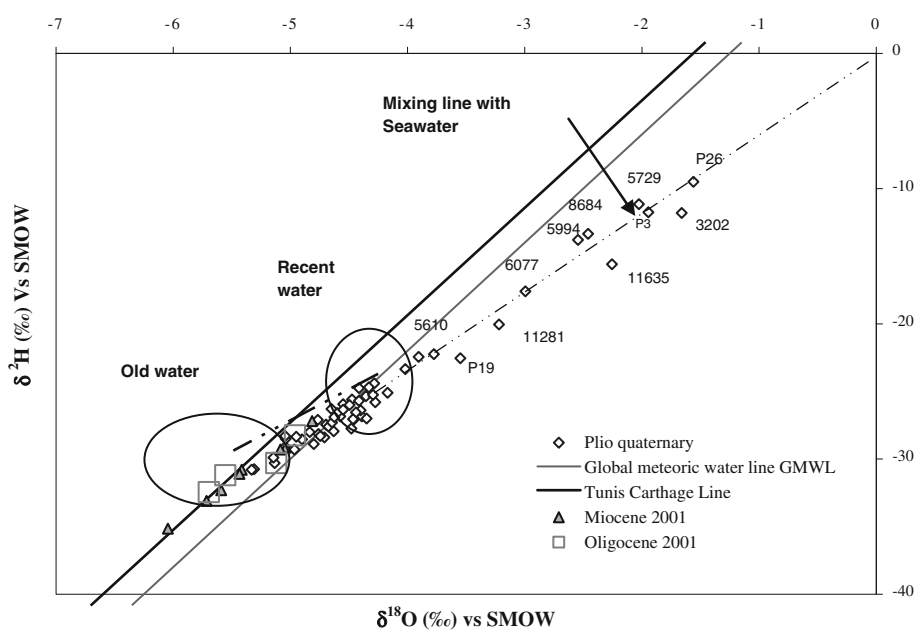
is most probable. The location of these water points, often near rivers, is compatible with a fast and recent recharge.

The second group was formed by the water enriched in ^{18}O and ^2H , which aligned on the mixing line of seawater, indicating a probable marine contamination. These wells are located on the piezometric depression area (P19, 11281, 11635, 8684, P3, 5729, 6077, 5610), except for two locations (3202, 5994). For the points closer to the first group, differentiating between mixture with salt water and evaporated water can be difficult.

The third group is mainly composed of deep Miocene and Oligocene groundwater, the ^{18}O contents of which vary between -6.05 and -4.82 ‰; thus, <-4.41 ‰ is the weighted average of rain in Tunis-Carthage (Celle-Jeanton et al. 2001). The Plio-quadernary waters of this group could result from a mixture of new and older waters (Karro et al. 2004; Dassi et al. 2005; Kamel et al. 2005; Ben Hamouda 2008).

- **The $^{18}\text{O}/\text{Cl}^-$ relationship** A separate study of ionic relationships and stable isotopes was not able to identify the origin of the water exactly. The combination of these two parameters is more explicit, especially the $\text{Cl}^-/^{18}\text{O}$ graph (Ma et al. 2006) (Fig. 8) that places the samples between different poles again. The first pole, around 10 mg/l for Cl^- and 4.4‰ V-SMOW for $\delta^{18}\text{O}$, is defined from the rainwater samples at Tunis-Carthage located about 40 km east of the study area and at practically the same altitude. The second pole is represented by Mediterranean waters, having a $\delta^{18}\text{O}$ content that corresponds to V-SMOW (0‰) and a Cl^- content of about 19,500 mg/l. The third pole is the water from the Miocene and Oligocene aquifers, with

Fig. 7 Isotopic content (^{18}O , ^2H) in aquifers of the eastern coast in 2001



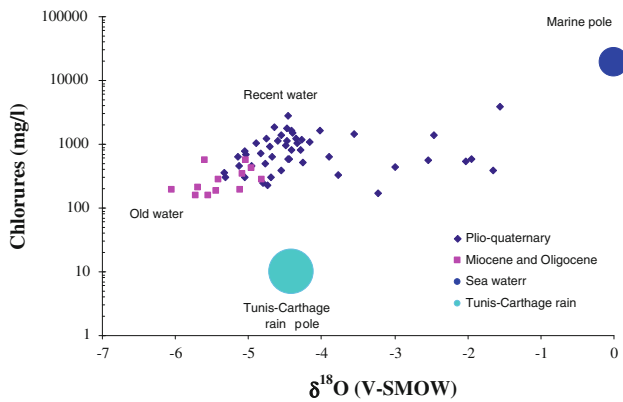


Fig. 8 $^{18}\text{O}/\text{Cl}^-$ correlation in the groundwater of the eastern coast aquifer of Cap Bon

lower mineralization and ^{18}O levels than the Plio-quadernary water.

Ten Plio-quadernary points are found between the rainwater and sea poles. They correspond to shallow wells in the Korba and Tafelloune region, very near the Mediterranean Sea, with a total mineralization nearing 5 g/l and which reaches 30 g/l in some places. Mixing with the seawater seems a more likely explanation than an eventual marking by evaporation, although the two processes could coexist. The other Plio-quadernary points have Cl^- levels varying between 300 and 2,000 mg/l and $\delta^{18}\text{O}$ levels from -5.5 to -4.0% V-SMOW. Their sometimes heavy mineralization cannot be understood from only one rainwater–seawater dipole.

- **Mixing ratios between fresh and saline water** Near the coast, it is possible to estimate the mixing fractions of seawater F (Table 2) and fresh groundwater in the Plio-quadernary aquifer. This estimation has been based on the calculation of the mass balance of the chloride (conservative element) (Abou Zakhem and Hafez 2007; De Montety et al. 2008). Theoretical mixing could be calculated in the following equation: $F = \frac{m\text{Cl}_{\text{sample}} - m\text{Cl}_{\text{fresh}}}{m\text{Cl}_{\text{sea}} - m\text{Cl}_{\text{fresh}}}$ where F represents the fraction of seawater in every sample and $m\text{Cl}_{\text{sample}}$, $m\text{Cl}_{\text{fresh}}$ and $m\text{Cl}_{\text{sea}}$ represent the concentration of chloride (mg l^{-1}) in the sample, freshwater and seawater, respectively. The contribution of seawater in the Plio-quadernary aquifer (Table 2) has been estimated to be between 4 and 10% and may reach a maximum of 70% depending on the location transposing heterogeneity from the salinization process in this region (Djabri et al. 2007).

Discussion and conclusion

Old measurements taken before 1980 (Ennabli 1980), typical of the natural state of the aquifer, show that the

shallow aquifer of the eastern coastal aquifer of the Cap Bon was less mineralized in downstream than upstream. This paradox implies that the recharge within upstream in the outcrop zones is complemented by a strong recharge in downstream by little mineralized water, probably coming from the fast infiltration of the water from the flooded river as it emerges on the plain. Recent observations (Ben Hamouda 2008) comply with this hypothesis. In the context of increasing mineralization in areas invaded by seawater, high fluctuations following years with heavy rainfall show the magnitude of the current recharge, as in 2003 and 2004 (annual rainfall of 510 and 820 mm, respectively).

On a smaller scale, the great spatial variability of piezometry and conductivity in the part closest to the sea indicates that there is not a general contamination of the groundwater, but rather a complex situation where the interpolations between the measured points remain delicate. The Plio-quadernary groundwater is thus subject to multiple influences, both climatic and anthropic, which disturb the system according to temporal dynamics.

The lack of correlation between Cl^- and NO_3^- levels, even for their highest levels, confirms that there is no one explanation for high mineralization. The particularly high nitrate contents come from a high agricultural contamination, facilitated by a significant development of the irrigation (29 values with more than 60 mg/l among the 48 values of 2001).

The lack of correlation between nitrate levels and thickness of the unsaturated area indicates that the entire region is affected by this pollution. The vertical transfer was sufficiently intense to reach the aquifer in large quantities. The observed contents result from the mix of runoff from an upstream contaminated in the saturated zone and runoff from an unsaturated zone, reinforced and contaminated on the surface by irrigation.

The study of the Na^+/Cl^- relationship did not show a clear distinction between the groups of water except in the most mineralized points. The $\text{Ca}^{2+}/\text{Mg}^{2+}$ relationship isolates some water points, which are already distinct in their Na^+/Cl^- relationship such as 11635, 11281, 11637 and 11828 with a molar relationship considerably <1 , most likely coming from a mix with seawater.

The Br^-/Cl^- ratio also identifies points, which seem to be contaminated by seawater. These points sometimes differ from those distinguished by the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio. These two approaches are complementary, but imperfectly discriminating.

The stable isotopes ^{18}O and ^2H also allow certain seawater contaminations to be identified. Thus, again, there is not total convergence with the other methods, but the results are much more precise. Moreover, closeness of rainfall values to those from the Plio-quadernary aquifer shows that the majority of groundwater has undergone

Table 2 Summary of the various approaches applied for the distinction of the origin of salinity

Sample no	Piez. Lev (m)	Salinity (mg/l)	Sea water F (%)	Na/Cl (mEq/l)	Ca/Mg (mEq/l)	Br/Cl (mEq/l)	Hydro	Seawater (%)	Isotopes	Na/Cl	Ca/Mg	Br/Cl	Origin of salinization
P1	33	2144	2.13	0.83	3.06	1.14E-03	NDN	PN	NDN	PY	NDN	PN	No seawater intrusion
P 3	1.2	2035	1.47	1.11	2.60	1.41E-03	PY	PY	PY	PN	PN	PY	Possible mixing with seawater
P19	3.5	3520	5.97	0.75	2.32	1.58E-03	PY	PY	NDY	NDY	PN	PY	Possible mixing with seawater
P26	8.3	8371	18.38	0.63	1.79	1.36E-03	PN	PY	PY	NDY	PN	NDY	Evaporation + dissolution
97	3.7	7296	12.84	1.11	1.54	1.63E-03	PN	PY	PN	PN	PN	PN	Evaporation + dissolution
892	-7.7	3469	6.45	0.61	1.88	1.85E-03	NDY	PY	PN	NDY	PN	PY	Possible mixing with seawater
996	13.6	2650	3.90	0.82	2.35	1.76E-03	PN	PN	PN	PY	PN	PN	No Seawater intrusion
1129	27.3	2067	2.57	0.93	2.15	1.78E-03	NDN	NDN	NDN	NDN	NDN	PN	No Seawater intrusion
3093	40.9	1265	0.03	0.77	4.12	1.85E-03	NDN	NDN	NDN	PY	NDN	PY	Freshwater, no seawater intrusion
3113	5.6	1153	0.00	0.86	36.08	1.44E-03	PN	NDN	NDN	PY	NDN	PN	Freshwater, no intrusion
3190	52.9	2451	3.16	0.84	3.13		NDN	NI	NDN	NDN	NDN		Dissolution by irrigation return flow
3202	47	1920	0.46	1.62	1.36	1.58E-03	NDN	NDY	NDN	NDN	NDN	PN	Evaporation
4814	102	3417	4.31	1.10	2.22	1.46E-03	NDN	NDN	NDN	NDN	NDN	PN	Evaporation
5610	-1.6	1293	0.14	0.90	1.83	8.30E-04	NDY	PY	NDY	PN	PN	PN	Very weak mixing with seawater
5729	10.9	1510	1.28	0.66	0.87		NDN	NDN	NDY	NDY	NDY		Very weak mixing with seawater
5743	28.8	2400	2.61	1.06	1.37		NDN	PN	NDN	NDN	NDN		Dissolution by irrigation return flow
5972	40.2	1485	0.47	0.60	8.21	1.63E-03	NDN	NDN	NDN	PY	NDN	NDN	Freshwater, no seawater intrusion
5994	25.8	1862	1.39	0.92	3.96		NDN	NDN	PY	PN	PN		Evaporation
6077	15.6	1613	0.73	0.84	4.53		PN	PN	PY	PY	NDN		Possible mixing with seawater
6686	38.1	1702	1.02	0.87	4.36		NDN	NDN	NDN	PY	NDN		Freshwater
8088	50.4	1958	1.76	0.82	4.57		NDN	NDN	NDN	PY	NDN		Freshwater, no seawater intrusion
8315	4.8	4762	8.22	0.93	1.22	1.41E-03	PY	PY	PN	PN	PN	PY	Possible mixing with seawater
8346	0.4	2323	0.84	0.92	3.28		PY	PY	NDN	PN	NDN		No seawater intrusion
8377	72.4	2010	0.84	0.92	3.28		NDN	PN	NDN	PN	PN		No seawater intrusion
8400	4.7	1971	2.02	0.88	2.42	1.65E-03	PN	NDN	NDN	NDN	NDN	NDN	Freshwater, no seawater intrusion
8403	10.4	3648	4.64	0.85	2.42	1.71E-03	NDN	PY	PN	PY	PN	PY	Possible mixing with seawater

Table 2 continued

Sample no	Piez. Lev (m)	Salinity (mg/l)	Sea water F (%)	Na/Cl (mEq/l)	Ca/Mg (mEq/l)	Br/Cl (mEq/l)	Hydro	Seawater (%)	Isotopes	Na/Cl	Ca/Mg	Br/Cl	Origin of salinization
8420	-0.4	2413	3.35	0.81	2.65	1.58E-03	NDY	PY	PN	NDY	PN	PY	Seawater intrusion
8647	2	1696	1.76	0.48	3.13	7.04E-03	NDN	NDN	NDN	PY	NDN	NDN	Freshwater, no seawater intrusion
8684	4	3232	5.53	0.92	1.27	2.04E-03	PY	PY	NDY	PN	PN	PN	Seawater intrusion
8737	0.8	3578	7.12	0.63	2.12	2.19E-03	PY	NDY	PY	PY	PN	PN	Possible mixing with seawater
8774	1.6	2995	4.72	0.60	1.23	1.37E-03	PY	PY	PN	PY	PN	NDY	Possible mixing with seawater
8820	40.6	1453	0.03	1.94	1.70	1.39E-03	NDN	NDN	NDN	NDN	NDN	PN	Freshwater, no seawater intrusion
8894	-2.8	2848	4.27	0.58	3.12		NDY	PY	PN	PY	PN		Possible mixing with seawater
10959	-2	1162	1.47	0.73	0.76		NDY	PN	PN	PY	PY		Possible mixing with seawater
10995	-0.2	3226	6.86	0.71	13.80		PY	PY	PY	PY	NDN		Possible mixing with seawater
10996	1.6	1023	0.32	0.52	5.48	1.30E-03	PY	NDN	NDN	PY	NDN	PN	Freshwater, no seawater intrusion
11186	3.7	3802	5.64	0.92	2.21	1.47E-03	PY	PY	PN	PN	NDN	PY	Possible mixing with seawater
11191	6.4	2355	4.72	0.64	1.33	2.03E-03	PN	PY	PY	PY	PN	PN	Possible mixing with seawater
11635	0.4	27160	70.64	0.82	0.44		NDY	NDY	NDY	NDY	NDY		Seawater intrusion
11637	0.8	10430	22.44	0.90	0.42		NDY	NDY	PY	PY	NDY		Seawater intrusion
11650	4.3	2331	2.72	0.93	4.95		PN	PN	PN	PY	PN		Dissolution, irrigation return flow
11829	6.8	2432	3.98	0.63	2.01	1.58E-03	PN	PN	PN	PY	PN	PY	Possible mixing with seawater
11269	-8.7	1702	1.54	0.68	1.82		NDY	PY	PN	PY	PN		Possible mixing with seawater
11281	1	36315	66.19	0.97	0.58		PY	NDY	NDY	PY	NDY		Seawater intrusion
11828	4.3	4090	7.63	0.58	0.57	1.68E-03	PN	NDY	PN	NDY	NDY	PY	Possible mixing with seawater
11869	3.2	858	0.00	0.99	1.89		NDN	NDN	NDN	NDN	NDN		Freshwater, no seawater intrusion
13143	-1.05	21050	70.4	0.5675	0.6667		NDY	NDY	NDY	NDY	NDY		Seawater intrusion
13207	-0.66	9960	27.7	0.6475	0.875		NDY	NDY	NDY	NDY	NDY		Seawater intrusion

NDY no doubt, yes, NDN no doubt no, PY possibly yes, PN possibly no, M no idea

neither high evaporate dissolution nor mixing with seawater.

The piezometry is evidently an indicator of overexploitation, but the geometry and hydrodynamic characteristics of the aquifer are such that the most depressed areas are not necessarily the most contaminated by seawater.

The relationship between $\delta^{18}\text{O}$ and Cl^- proves that evaporation has very limited effects, whereas groundwater salinization is mainly due to seawater intrusion. Seawater intrusion is more pronounced in the central part of the plain than in the north and south of the study area.

Table 2 summarizes the result of the different approaches, where the lines show the water points and the columns show the geochemical methods and hydrodynamic information. This table indicates whether the method gave information about the origin of mineralization for that point and the degree of certainty of the information (no doubt yes: NDY, no doubt no: NDN, possibly yes: PY, possibly no: PN, no idea: NI). The criteria are as follows: presence of wells in a piezometric depression area for hydrodynamics, fraction of seawater F greater than 1%, enriched isotopes, and Na^+/Cl^- , $\text{Ca}^{2+}/\text{Mg}^{2+}$, Br^-/Cl^- ratio close to the marine ratio. The comparison between the different approaches shows that none of the methods is reliable and that it can lead to contradictory results.

Even in an apparently simple case as the groundwater of the eastern coastal aquifer of Cap Bon, the hydrogeologic study of the Mediterranean coastal aquifers requires a careful and critical step. The comparison of multiple hydrodynamic and geochemical approaches is essential to disentangle the processes, which are superimposed and end up together in the decrease of piezometry and the increase of salinity.

However, the variability of the results obtained according to these methods underlines the difficulty of interpretations. The overlapping of different processes and limitations related to the data and interpretations make particularly delicate the quantification of the evolutions of the next few decades.

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