

# Impact of agricultural activity and lithology on groundwater quality in the Merdja area, Tebessa, Algeria

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**Abstract** This work presents results of the hydrogeological and hydrochemical studies on groundwater samples from the alluvial aquifer of Merdja in Tébessa, located in the Western part of this town. Its groundwater resources are used mainly for crop irrigation in an agriculture dominated area. Hydrochemical and water quality data obtained through a sampling period (December 2008) and analysis program indicate that nitrate pollution can be a serious problem affecting groundwater due to the use of nitrogen (N) fertilizers in agriculture. The concentration of nitrate in groundwater ranged from 19 to 281 mg/l. Considerable seasonal fluctuations in groundwater quality were observed as a consequence of agricultural practices and other factors such as annual rainfall distribution and the wadi El Kebir flow regime. The chemical composition of the water is not only influenced by agricultural practices, but also by interaction with the alluvial sediments. The dissolution of evaporites accounts for part of the  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ , but other processes, such as calcite precipitation and dedolomitization, also contribute to groundwater chemistry.

**Keywords** Groundwater · Hydrochemistry · Nitrate pollution · Wadi El Kebir, Algeria

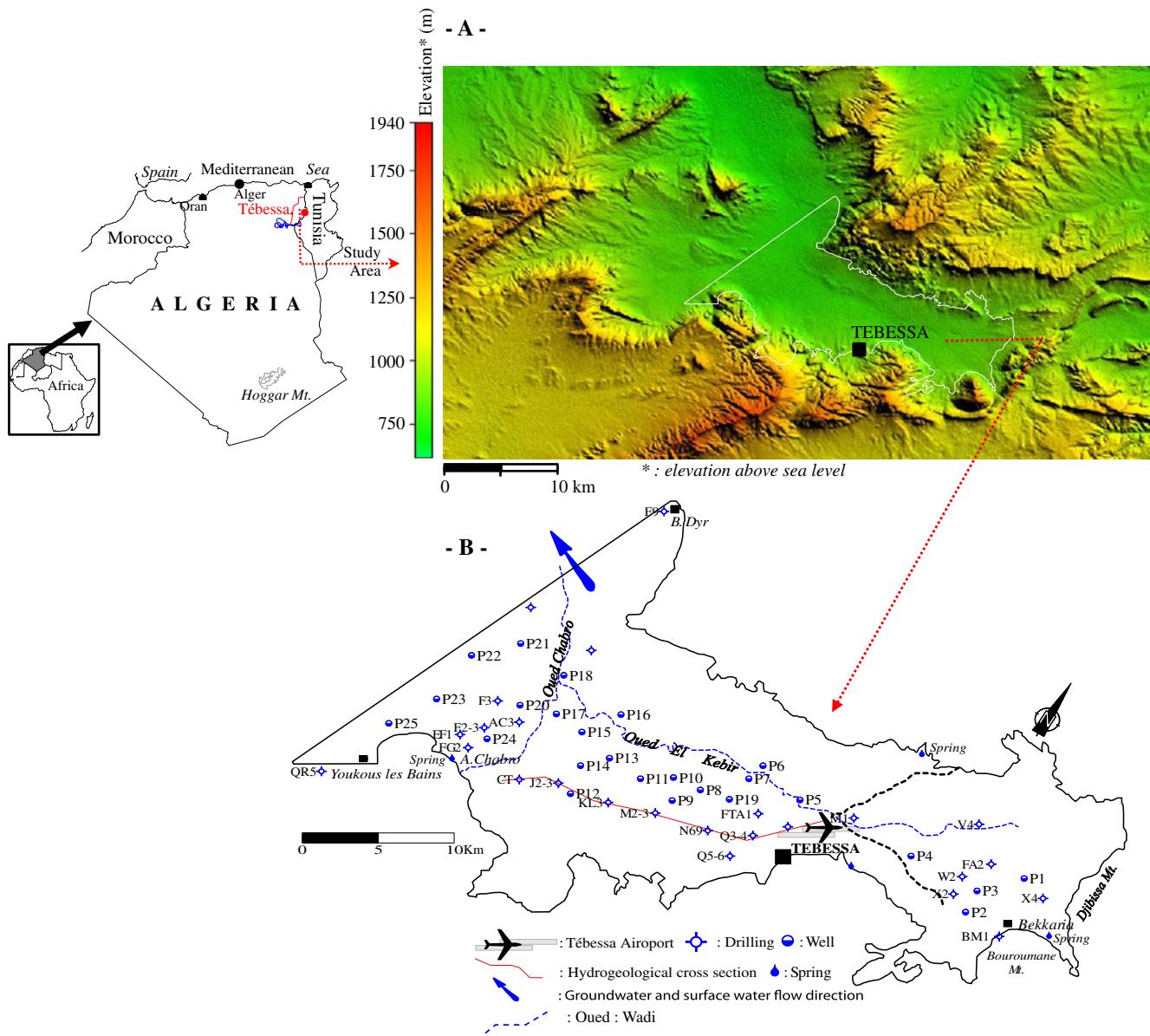
## Introduction

Agriculture can have a significant impact on the quality of groundwater. Nitrate and chloride pollution of surface water is of high concern as it may have negative impacts on water supply and ecosystems (Postma et al. 1991; McNeely et al. 1979; Rouabchia et al. 2004 and 2008a, 2008b, Baali et al. 2007). High nitrate concentrations in water serving as a source for drinking water is a serious health problem, being known for many years as the cause of blue baby syndrome and related to increased levels of diarrhea of children (Fehdi et al. 2008, Hamilton and Helsel 1995).

Return flows from irrigated agriculture may increase the salt, nitrate, and chloride concentrations of the receiving water bodies, limiting their agricultural, industrial, urban, and ecological uses. Irrigated agriculture in semi-arid areas significantly contributes to crops productivity, stability, and diversification. However, the return flows from irrigated agriculture are considered a major diffuse contributor to the contamination of surface and groundwater bodies (Rouabchia et al. 2004).

The area of study is near the city of Tebessa in eastern Algeria (Fig. 1a, b). This area lies in the semi-arid region of Algeria and is susceptible to the various threats common in both growing urban areas and developing agricultural areas. The city of Tebessa and the surrounding villages (Bekkaria and Youkous les bains: Hammamet) have seen a great deal of growth in the past decade, with the establishment of new industries and farms. The most important economic activity of the area is agriculture. Large amounts of synthetic nitrogen fertilizers, such as urea 46%, ammonium nitrate 33.5%, liquid fertilizer N-32%, or commercial complex

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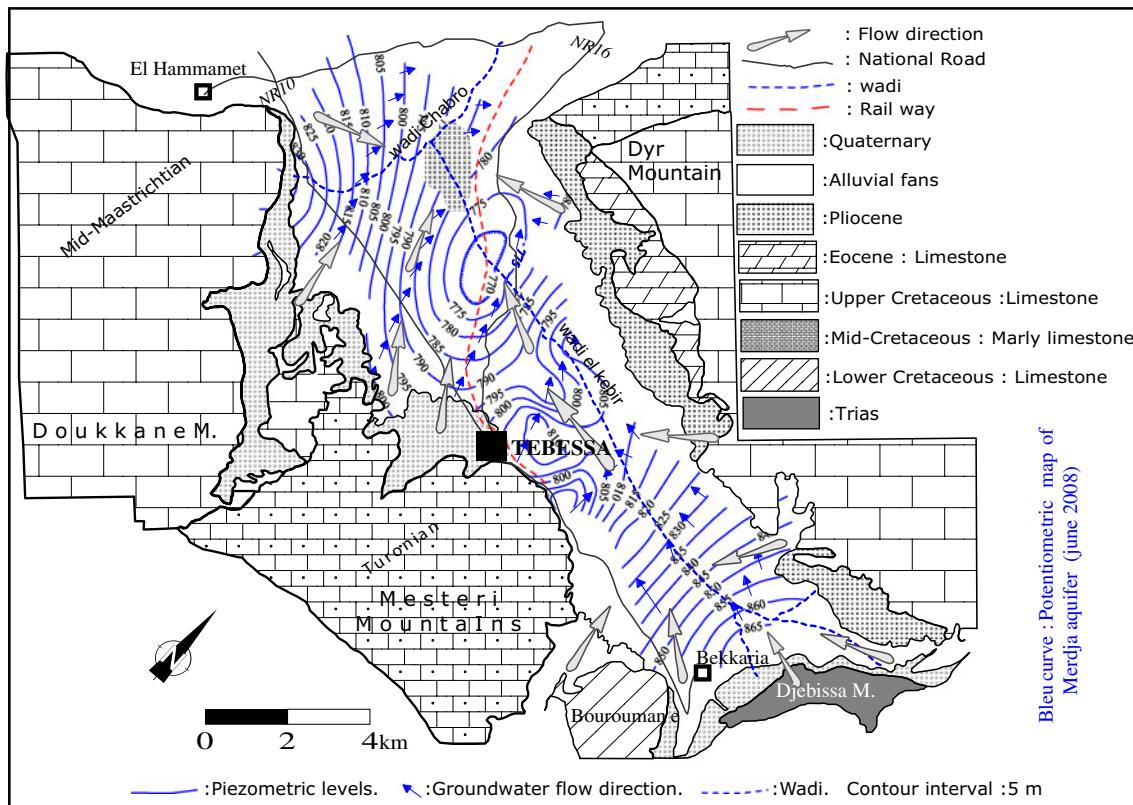


**Fig. 1** Location of the study area in Eastern Algeria. **a** Topographic map, **b** sampling shallow wells

fertilizers with different proportions (%) of nitrogen, phosphorous, and potassium [(N=15, P<sub>2</sub>O<sub>5</sub>=15, K<sub>2</sub>O=15), (N=8, P<sub>2</sub>O<sub>5</sub>=15, K<sub>2</sub>O=15), and (N=9, P<sub>2</sub>O<sub>5</sub>=18, K<sub>2</sub>O=28)] are applied during farming season (summer and autumn). The amount of nitrogen fertilizers used varies significantly within the study area depending on the type of crop, the amount of nitrogen in the irrigation water and soil, and also on each farmer's practices. The consequent paucity of information makes it difficult to establish a nitrogen balance in the aquifer. In addition to agricultural practices, other non-point sources of nitrogen include precipitation and irrigation water containing nitrogen. Point sources of nitrogen such as septic tanks and dairy lagoons are not significant in this area.

The main aims of this study are: (1) to identify the spatial and temporal trends of nitrate in groundwater and (2) to evaluate the characteristics, spatial distribution, and variations in groundwater chemistry as a result of agricultural practices and water–sediment interactions within the aquifer.

The Tébessa area contains two aquifers: the limestone aquifer and the alluvial aquifer. In general, the shallow groundwater in Merdja area is found in the alluvial fan deposits from plio-quaternary age (Fig. 2). This aquifer overlies geologic formations consisting of cenomanian marly layers. The recharge of this alluvial aquifer is combined and is done from: (1) highlands of Dyr Bouroumane on the East and Doukkane on the West (precipitation



**Fig. 2** Geological and hydrogeological boundary conditions map of the study area

infiltrating through alluvial fans where the mountain range meets the plain); (2) from losing streams; and (3) through cross-formational flow.

Annual precipitation in the studied area ranges from 200 to 320 mm (Rouabchia et al. 2008a, 2008b); thus, this is considered to be a semi-desert area. Summer temperatures can reach 45°C. This situation of dryness accentuates the drawdown of water resource especially during the last decade because the renewal of this resource is very weak. Dryness generates sometimes very unfavorable effects on groundwaters. (Aquifer refill decreases considerably whereas the exploitation increases). The dry climate, atmospheric dust, and low precipitation can also affect the water quality generally causing increased salt content (Fehdi et al. 2008).

#### Geological and hydrological setting

The geology of the studied area was investigated by several authors (Blés and Fleury 1970; Vila 1980). The micro-paleontological and biostratigraphical analyses have showed that, from the stratigraphical point of view, the studied area includes the plio-quaternary tectonic depression of Tebessa; this depression separates the highlands of Dyr situated in the North from the Doukkane and Mestrie highlands located in the South. Most of the area is of

Cretaceous age (Fig. 2), and forms a series of anticlines and synclines. The stratigraphic consists of alternating sequence alternation carbonate formations of limestones, marly-limestones, and argillaceous marls. The plio-quaternary and quaternary terrains occupy the central part; they are consisted by actual and recent alluvial deposits, conglomerates, gravels, sandstones, etc. Analysis of the hydrostratigraphic column of the studied area suggests the presence of two aquifers including the formation of plio-quaternary age (Djabri 1987). This large alluvial aquifer occupies the major part of the tectonic depression, limited at the North and at the South by two great faults of W-E orientation (Fig. 2). It is composed of diverse deposits such as alluvial fans, silts, calcareous crust, conglomerates, and gravels. This aquifer plays an important role in the drinking water supply for the local population, where it undergoes a strong solicitation, which generates an anthropogenic pollution.

Different wells have been drilled into the alluvial aquifer, supplying water mainly for irrigation, show groundwater levels from approximately 20 to 30 m in depth. Average water level fluctuations are not greater than 1.5 m between dry and wet seasons. The general direction of groundwater flow is from east to west. Average permeability in the sandy levels is around  $10^{-3}$  m/day (Djabri 1987). The aquifer is

mainly recharged by precipitation, irrigation water, and El Kebir Wadi. At some places the wadi may recharge or drain the aquifer depending on several factors such as river flow, water table, and the permeability of the river bed materials.

Hydrogeological cross-section (Fig. 3) shows that the depth to the top of the water table vary between 25 and 30 m, this groundwater level near to surface, causes a degradation of the alluvial aquifer waters by the various external agents (anthropogenic pollution, evaporation, etc.).

## Materials and methods

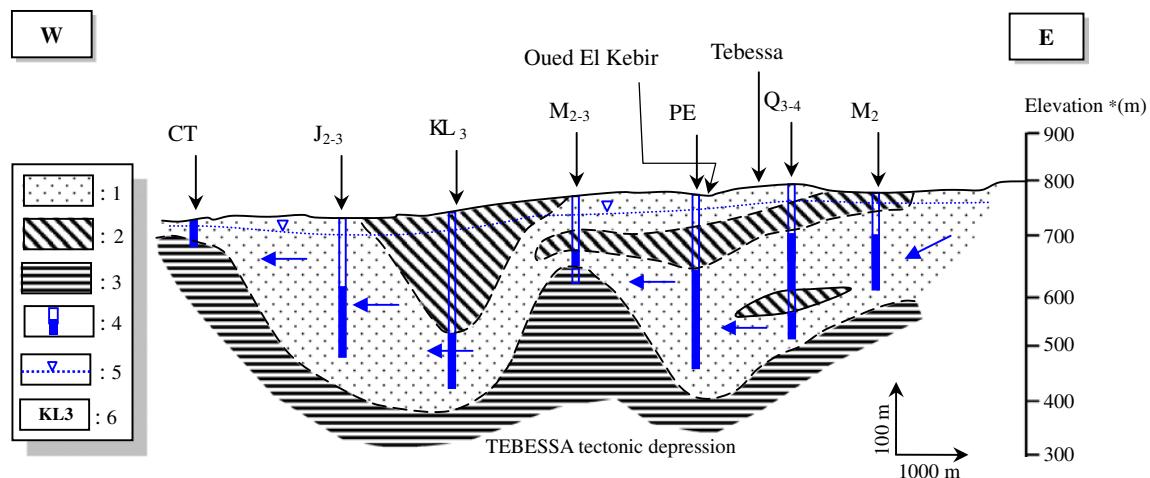
The hydrochemical properties of groundwater samples collected from the quaternary aquifer system are showed in Table 1. The sites which samples were taken are shown in Fig. 1b. The experimental data, corresponding to December 2008, were obtained from field surveys and from chemical analyses performed in the laboratory. Portable equipment was used to obtain in situ readings of temperature, pH, and electrical conductivity (EC). At the same time, samples of non-acidified water in 500 ml polyethylene bottles were taken. The measurement of  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  was carried out in the shortest time practicable, although the field campaigns normally took 3 or 4 days; during this period, the samples were kept at a low temperature in a portable refrigerator. The  $\text{HCO}_3^-$  content was determined as the total alkalinity, by titration with  $\text{HCl}$  0.05 N and methyl orange as indicator. The cations were analyzed by atomic absorption spectrometry (Ca and Mg) and by emission spectrometry (Na and K). A visible light spectrophotometer was used to analyze  $\text{SO}_4^{2-}$  by

turbidimetry and the  $\text{SiO}_2$ , by colorimetry. The concentrations of  $\text{Cl}^-$  ions were determined by argentometric titration, using  $\text{AgNO}_3$  0.01 N and 5%  $\text{K}_2\text{CrO}_4$  as indicator.

The hydrochemical calculations were performed using the AQUACHEM program (Calmbach 1997), which makes it possible, in a straightforward way, to use of PHREEQC (Parkhurst and Apello 1999). The computer processing of these hydrochemical data had a main objective: determination the saturation indices of calcite, dolomite, and gypsum, and the partial equilibrium pressure of  $\text{CO}_2$ .

## Results and discussion

The physico-chemical and chemical data of all the investigated groundwater are summarized in Table 1. According to the analytical data, parameters values range widely except for the pH and dissolved oxygen (DO) and nitrate concentrations. DO and pH values increase slightly eastwards up to a maximum value of 8.6 mg/l and 7.92 respectively, whereas nitrate concentration increases westwards, with a maximum of 281 mg/l in December 2008. Significant changes in water quality occur along the river course due to the influence of its tributaries, wastewater disposal, agricultural activities, and large seasonal variations in the discharge rate of the Merdja plain. Variations in selected water quality parameters ( $\text{EC}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Na}^{2+}$ ) along the Merdja plain are illustrated in Fig. 4. In general, water quality becomes considerably worse downstream of the Merdja plain due to a significant increase in  $\text{Cl}^-$  ( $>200$  mg/l) and  $\text{SO}_4^{2-}$  ( $>250$  mg/l) concentrations. This is attributed to the Triassic unit rich in evaporites.

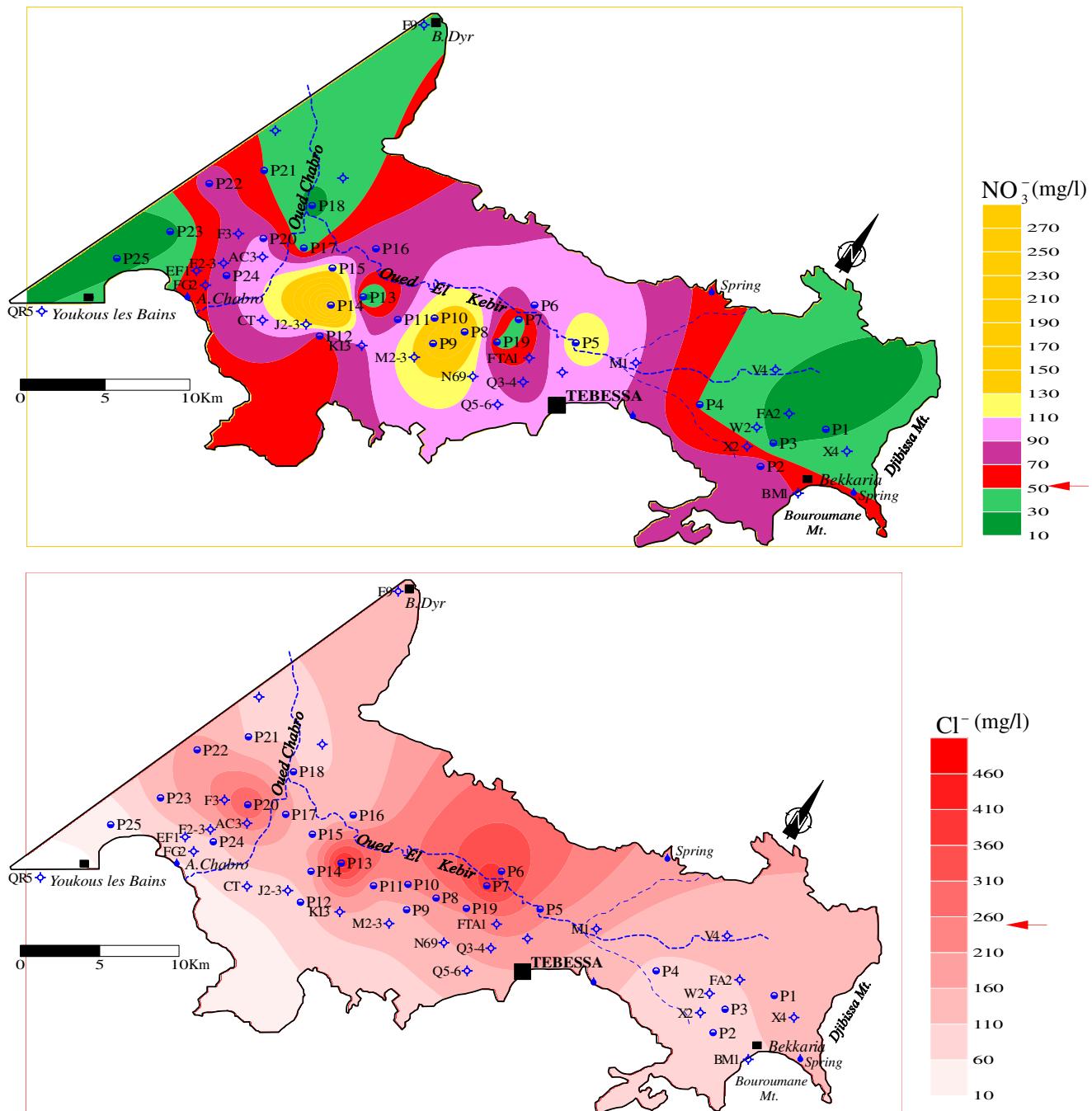


**Fig. 3** Hydrogeological cross-section through the Merdja plain. 1 Permeable zone (marly-limestones, alluvial fans, silts, calcareous crust, conglomerates, and gravels). 2 Impermeable zone (clay and marl). 3 Marly bedrock. 4 Screened interval. 5 Piezometric head, 6 well name. \* Elevation above sea level. E East, W West

**Table 1** Chemical composition (in mg L<sup>-1</sup>) of groundwater from the Merdja aquifer

well	T (°C)	pH	TDS (Mg L <sup>-1</sup> )	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>2-</sup>	Sr <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	NH <sub>4</sub>	DO	HCO <sub>3</sub> <sup>-</sup>	EC (µS/cm)
1	17	7.82	589	96	100.9	957.45	02.53	129	157	0.07	01.10	27	<0.1	7.46	258	682	
2	21.2	7.71	824	112	163.0	304.16	<0.01	104	102	0.11	05.86	88.5	0.12	2.30	4.37	321	784
3	12.9	7.81	881	76	135.8	196.6	25.73	92	129	1.55	00.53	24.8	2.22	1.23	7.50	523	1,272
4	14.5	7.72	377	76	90.21	120.55	01.2	97	86	0.07	00.86	48.4	0.51	2.54	7.20	336	398
5	16	7.84	1,071	109	132.82	170.5	07.80	226	329	0.13	02.80	126.5	3.21	6.04	8.6	151	2,320
6	18.4	7.80	920	148	99.30	83.14	05.27	360	168	0.11	01.60	95.5	3.66	1.65	6.23	166	2,682
7	17.8	7.73	1,039	168	128.31	56.02	02.70	397	343	0.12	03.88	40.74	0.40	0.25	6.25	275	1,324
8	19.4	7.72	2,176	125	220.91	353.2	10.22	221	243	0.23	07.38	179.7	1.90	6.12	7.14	288	3,250
9	19.5	7.80	922	154	212.90	469.17	04.93	148	158	0.05	10.45	163.8	0.11	5.41	8.15	198	530
10	18.3	7.71	1,400	72	112.93	268.67	06.66	223	610	0.27	02.67	135.4	0.26	4.02	4.56	193	2,553
11	17	7.23	676	114	95.65	549	03.62	176	242	0.15	3.12	87	0.30	4.89	8.21	199	2,859
12	20.6	7.80	432	76	90.22	206	01.20	97	86	0.07	2.25	59	0.20	1.04	6.54	180.9	539
13	18.1	7.3	767	84	91.70	507	03.43	450	392	0.09	0.48	19	0.30	2.36	6.21	188.3	539
14	11.9	7.6	627	139	99.21	608	04.07	153	186	1.56	1.47	281	0.40	5.20	5.14	142	1,606
15	18.3	7.09	460	86	91.46	386	02.95	129	282	0.18	0.63	125	2.50	1.27	7.34	60.8	1,766
16	17.5	7.37	737	96	101.0	575	02.53	129	257	0.11	5.86	89.1	2.41	4.32	6.12	112	2,784
17	15.6	7.14	988	188	128.0	932	04.82	177	258	0.19	1.52	38	1.14	4.12	5.89	148	1,428
18	16.5	7.23	563	156	84.70	291	03.75	115	51	0.1	0.75	22	0.20	2.15	6.54	175	833
19	16.9	6.91	1,079	202	134.21	113	07.12	223	346	0.09	0.67	43	0.60	2.17	7.56	191	590
20	17	7.53	571	148	104.0	384	02.98	329	300	0.05	1.29	94	0.60	4.65	8.02	336	1,031
21	14.8	7.25	1925	112	163.0	304	00.01	104	102	0.07	0.86	49.2	0.50	1.58	7.33	151	398
22	15.5	7.61	845	84	1,29.0	225	04.05	182	241	0.12	0.82	81.2	0.10	3.65	4.69	166	802
23	16.5	7.21	600	177	109.0	325	03.67	136	100	0.07	0.78	21	0.40	3.14	7.21	275	808
24	16.3	7.92	584	163	70.90	139	15.60	96	58.7	0.03	0.9	84.2	<0.10	2.59	5.93	288	709
25	13.9	7.02	1,410	186	143	116	10.50	24.5	58	0.15	3.12	27	<0.10	1.04	7.12	198	682

TDS total dissolved solids



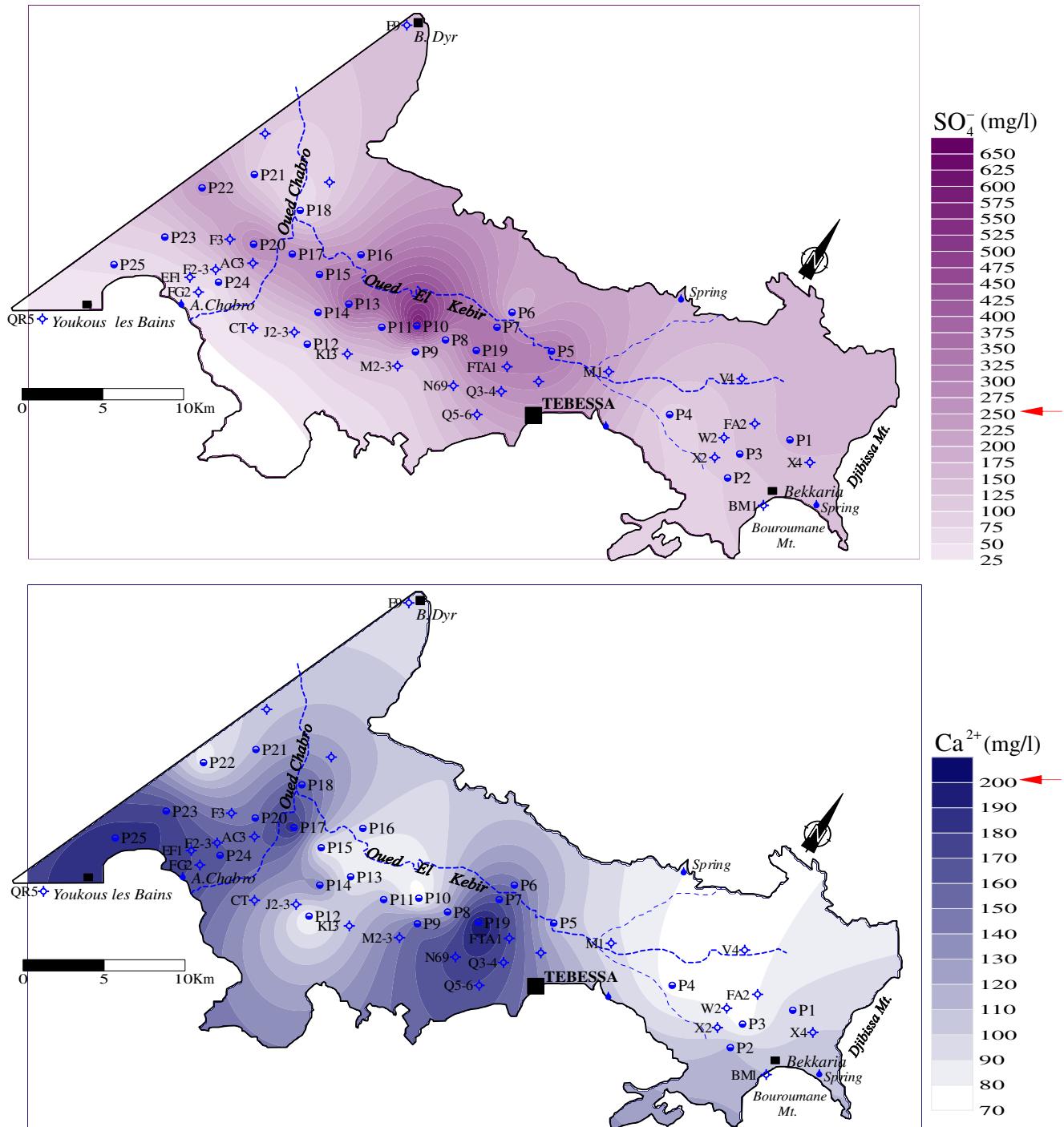
**Fig. 4** Map of some major ions in groundwater. Data from December 2008

### Hydrochemistry

Results of analyzed parameters in groundwater samples are given in Table 1. Temperature ranged from  $11.9^\circ\text{C}$  to  $21.2^\circ\text{C}$  and pH values were near neutral to slightly basic, with an apparent increase in pH towards the eastern part of the aquifer, where the maximum value of 7.92 was reached. The other quality parameters have wider ranges due to

spatial changes in the lithology of the alluvial sediments that constitute the aquifer and seasonal changes in fertilizer application and irrigation practices.

Two hydrochemical facies identified are  $\text{Ca}-\text{Mg}-\text{SO}_4-\text{HCO}_3-\text{Cl}$  and  $\text{Na}-\text{Ca}-\text{Mg}-\text{Cl}-\text{SO}_4$  (Fig. 5).  $\text{Ca}-\text{Mg}-\text{SO}_4-\text{HCO}_3-\text{Cl}$  type was found upstream (Bekkaria sector). Downstream, groundwater evolves to  $\text{Na}-\text{Ca}-\text{Mg}-\text{Cl}-\text{SO}_4$  types along the flow path. That change of facies is



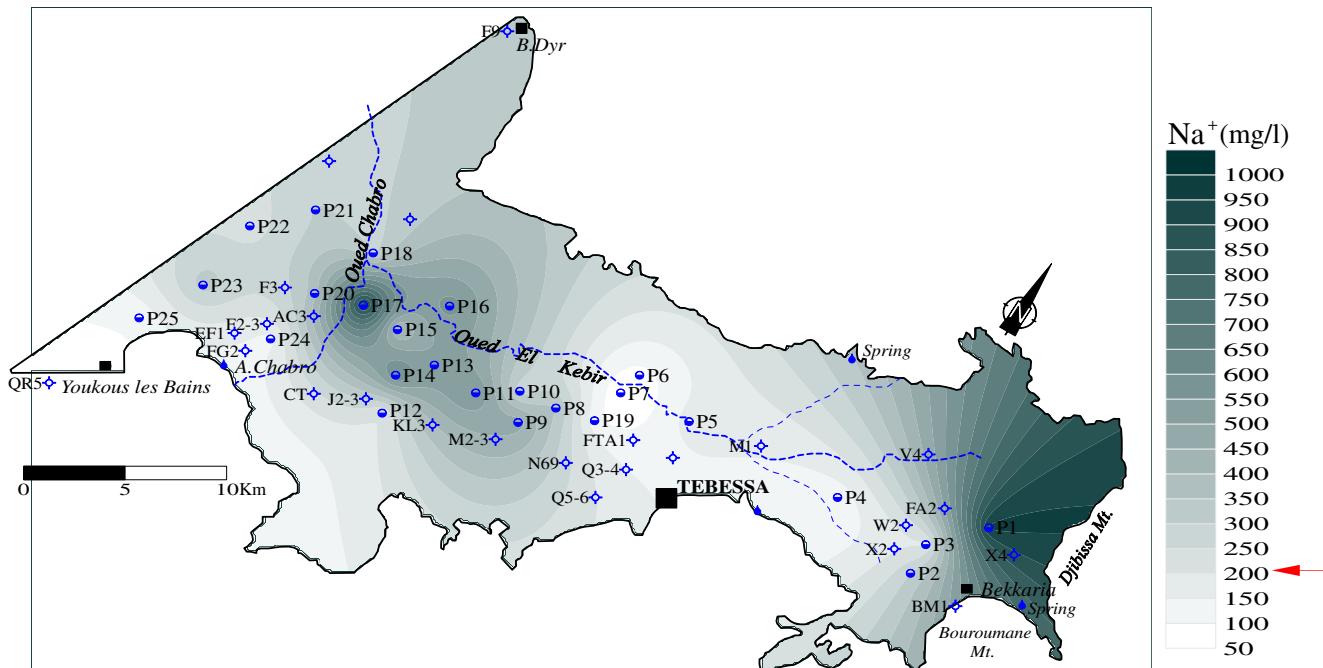
**Fig. 4** (continued)

accompanied by a gradual increase in the groundwater total dissolved solids (TDS) and is mainly controlled by evaporites dissolution present in the Triassic unit.

The spatial distribution of the values of EC,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ , and  $\text{Na}^+$  in groundwater in December 2008 shown in Figs. 6 and 4. These maps provide a basis for making area-wide generalizations concerning the distribution of water quality parameters.  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  spatial

distribution patterns are very similar, and show that the dissolution of evaporites significantly affect groundwater chemistry. Mention should be made of the high concentrations of  $\text{Cl}^-$  ( $>250 \text{ mg/l}$ ),  $\text{Na}^+$  ( $>200 \text{ mg/l}$ ),  $\text{SO}_4^{2-}$  ( $>350 \text{ mg/l}$ ), and  $\text{Ca}^{2+}$  ( $>200 \text{ mg/l}$ ) in wells located between Tébessa and Chabro wadi and downstream of the Ain Chabro.

A high correlation is also observed between  $\text{Sr}^{2+}$  and  $\text{SO}_4^{2-}$  ( $n=25$ ;  $r=0.855$ ;  $p<0.01$ ; Fig. 7), which suggests the



**Fig. 4** (continued)

dissolution of strontium sulfate (celestite; often associated with gypsum, anhydrite, and halite) as the main source of strontium.

Celestite deposits occur in Triasic unit of Djebissa Diapir. The main mineralization consists of granular celestite nodules. Dolomite, calcite, quartz, and gypsum are associated to celestite in secondary mineralizations (Djabri, 1987).

Other sources of sulfate in groundwater may be agricultural practices, although fertilizers containing sulfate are not commonly used in the study area.

The presence of carbonate rocks such as calcite and dolomite in the sediments determines the high  $\text{HCO}_3^-$  concentrations throughout the aquifer, which range between 60.8 and 523 mg/l. The spatial distribution of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations in groundwater is determined by the dissolution/precipitation of calcite and dedolomitization processes, as discussed below. Potassium concentrations are low (mean value of 5.72 mg/l) and show no significant changes across the basin. The source of potassium in groundwater is likely to be the weathering of K-feldspar present in the sediments and the application of synthetic fertilizers.

#### Impact of agriculture on groundwater

Within the study area, agricultural activities that involve the application of urea, ammonium nitrate, liquid fertilizer N-32%, and other commercial complex fertilizers are the main source of elevated nitrate concentrations in groundwater (up to 281 mg/l). About 56% of the samples have nitrate

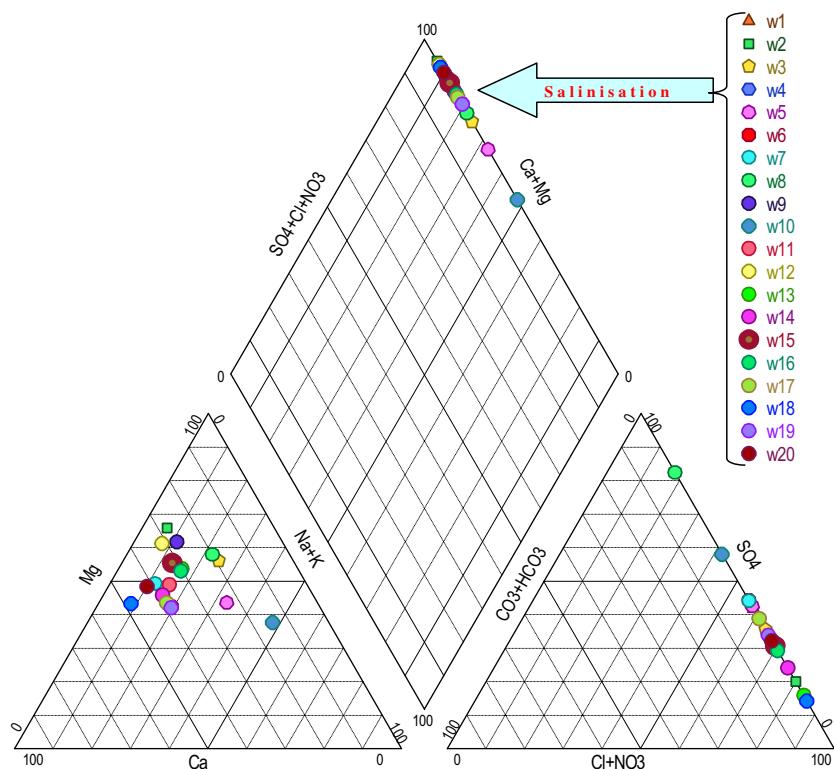
concentrations that exceed the drinking water limit of 50 mg/l (WHO 2006), with an average nitrate concentration in the groundwater of 82 mg/l. As illustrated in Fig. 4, anomalously high  $\text{NO}_3^-$  concentrations ( $>100$  mg/l) are found in irrigation wells located between Aeroport and Chabro wadi, where there is heavy agricultural activity above the aquifer and considerable amounts of synthetic fertilizers (300–600 kg/ha/year) are applied during the farming season. Nitrite usually occurs in small quantities in groundwater, is unstable in the presence of oxygen, and occurs as an intermediate form between ammonia and nitrate or nitrite and nitrogen gas (McNeely et al. 1979).

$\text{NO}_2^-$  concentrations vary between <0.1 (detection limit) and 3.66 mg/l, and  $\text{NH}_4^+$  concentrations vary between <0.1 (detection limit) and 6.12 mg/l. Phosphorous is also a component of complex synthetic fertilizers widely applied to farming land. The proportion of  $\text{P}_2\text{O}_5$  in the applied fertilizers varies between 15% and 18% (150–180 g of  $\text{P}_2\text{O}_5$  in each kilogram of fertilizer).

However, phosphate was not detected (concentrations below the detection limit: 0.1 mg/l) in groundwater. When phosphate is added to a soil, its concentration in solution initially declines very rapidly. This is followed by a more gradual decrease in solution concentration that can continue for weeks. Under aerobic conditions, adsorption on the surface of iron and aluminum hydroxides coating clay-sized particles controls the amount of phosphate in solution (Patrick and Khalid 1974; Elrashidi and Larsen 1978).

The concentration of dissolved oxygen in groundwater (mean value of 6.69 mg/l) indicates the presence of aerobic

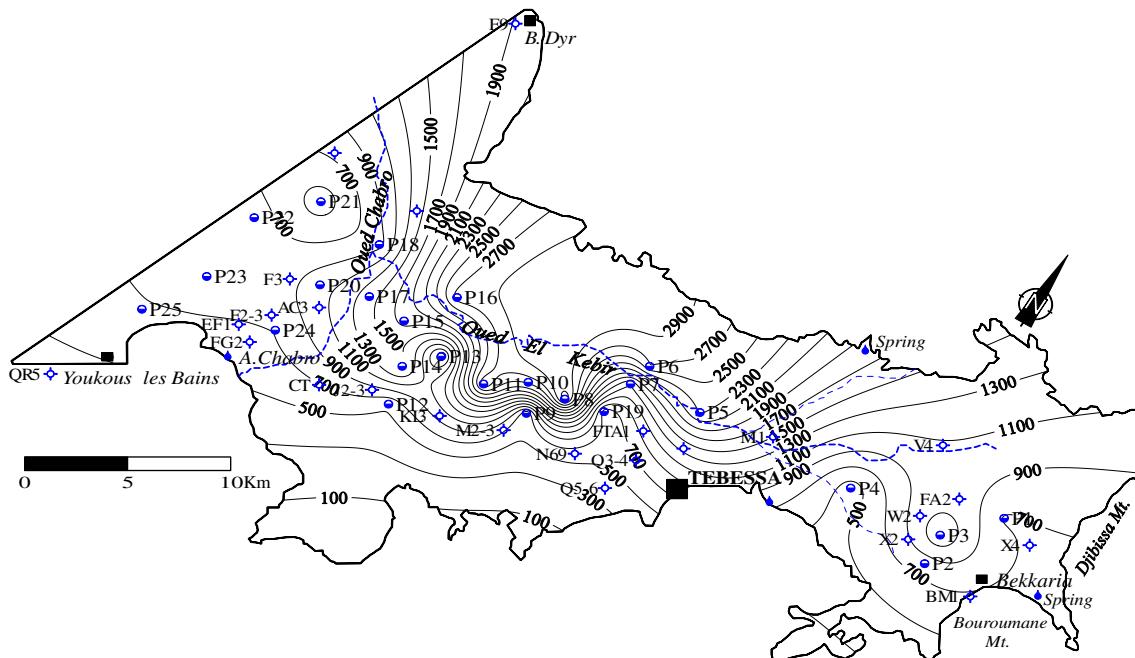
**Fig. 5** Piper diagram of the shallow aquifer groundwater



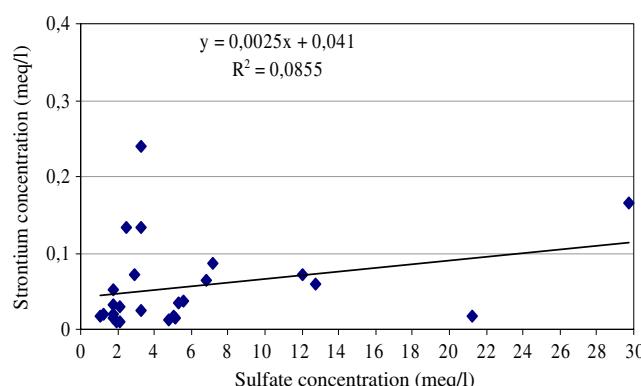
conditions in the aquifer and, therefore, the aforementioned mechanism might be the main factor leading to the low phosphate concentrations in the groundwater (McDonald et al. 2001).

The application of liquid fertilizer N-32% (N32) through fertilization is a common practice during the growing

season (June–July) in the area, which contains 16% urea, 8% ammonium, and 8% nitrate. Several studies have reported that a reduction in the proportion of NO<sub>3</sub><sup>−</sup> in applied fertilizers can lead to a considerable decrease in the potential for NO<sub>3</sub><sup>−</sup> leaching (Baali et al. 2007). The amount of N32 applied varies between 30 and 50 m<sup>3</sup>/ha/year



**Fig. 6** Distribution of EC ( $\mu\text{S}/\text{cm}$ ) in groundwater. Data from December 2008



**Fig. 7** Correlation between strontium and sulfate concentration in groundwater. December 2008

depending on the crop and on each farmer's practices (Rouabchia et al., 2008a, Rouabchia et al. 2008b).

A highly permeable, alluvial aquifer provides favorable conditions for the vertical transport of oxygen to deeper parts of the aquifer (Hamilton and Helsel 1995; Kraft et al. 1999; Nash and McCall 1995). Consequently, the alluvial aquifer of the Merdja plain is aerobic throughout its depth, with a mean DO concentration in groundwater of 6.69 mg/l. Under these conditions, urea and ammonium are readily transformed into nitrate. The nitrification rate of ammonium is very fast under aerobic conditions (15–20 days at 20°C; Kpomblekou and Killorn 1996). Therefore, infiltration of nitrogen-rich waters into the aerobic groundwater system seems to be the major cause of high nitrate concentrations in groundwater.

#### The spreading of the nitrate front

Nitrate concentration in groundwater depends on the hydrogeological conditions and the availability of electrons donors for denitrification (Postma et al. 1991). In the unconfined shallow aquifer (a few meters deep), the decrease in nitrate with depth can be due to the process of the reduction of nitrate by oxidation of organic matter within the sediments (Gillham and Cherry 1978). In deeper, unconfined aquifers (water table depth more than 10 m) small available amounts of labile organic carbon are not sufficient to support the denitrification process (Starr and Gillham 1993). If the later is the case of Merdja aquifer, denitrification does not take place, and  $\text{NO}_3^-$  behaves as a conservative chemical factor (see Fig. 4). The use of second Fick's law (Appelo and Postma 2005; Appelo et al. 1990; Appelo and Postma 1993; Appelo 1994; Appelo and Postma 1999), under specific boundary conditions could provide the appropriate model to estimate the transport of  $\text{NO}_3^-$  and furthermore to estimate the propagation of groundwater contamination. In Merdja plain the distance of the first 500 m from the continuous "source" a

main pollution spread of 0.201 m/day if  $v$  (groundwater velocity) =  $4,6 \cdot 10^{-6}$  m/s,  $D_f$  (diffusion coefficient) = 0,  $D_L$  (coefficient of the longitudinal dispersion) =  $10^{-6}$  m $^2$ /s (calculated using PHREEQC version 2, Parkhurst and Appelo 1999).

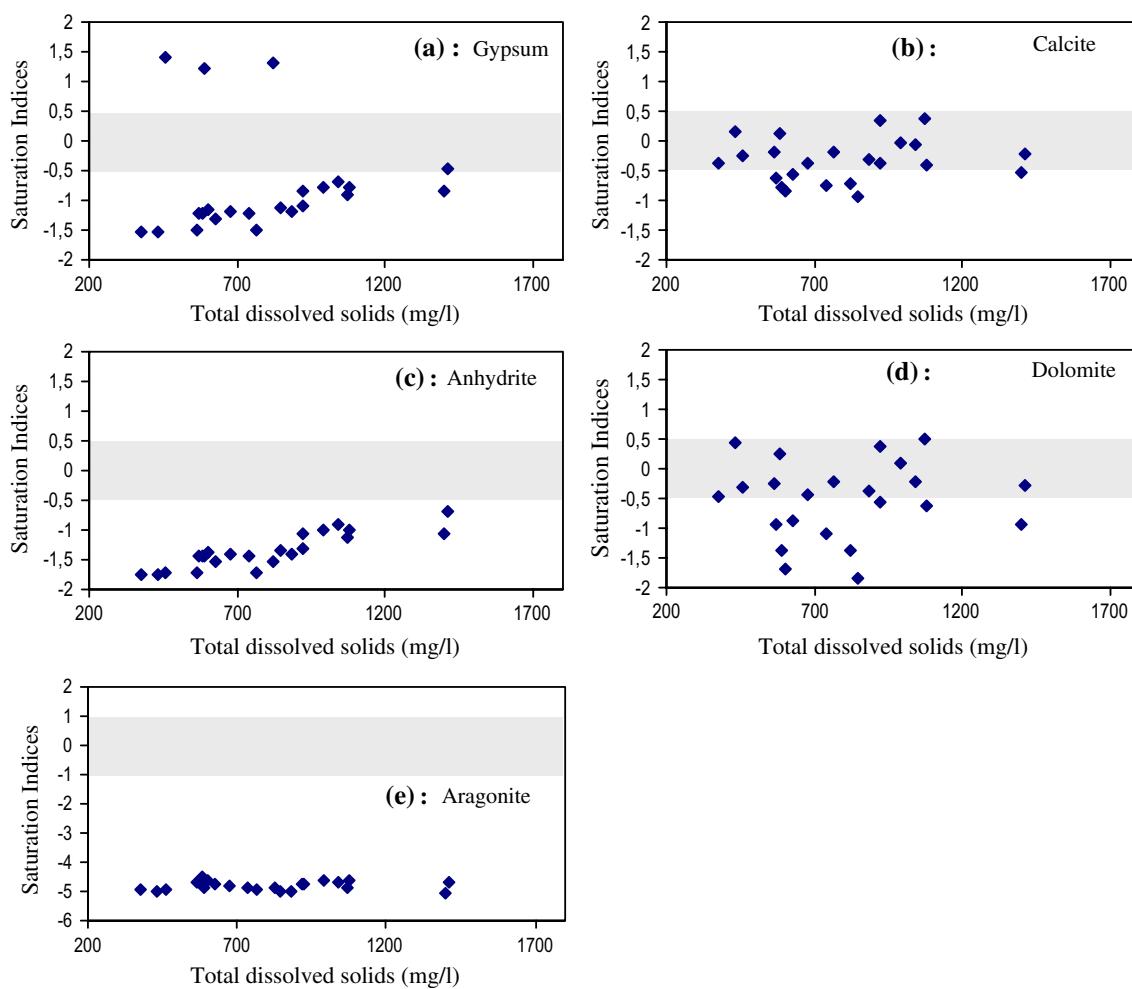
#### Water–rock interaction process

Interaction between groundwater and surrounding host rocks are believed to be the main process responsible for the observed chemical characteristics of groundwater in the Merdja plain. Evaluation of such process requires the description of the mineral assemblage of the rocks in which water is found, and the identification of chemical reaction responsible for the geochemical evolution of groundwater. From available studies in the literature, such reactions generally include chemical weathering of rock-forming minerals, dissolution–precipitation of secondary carbonates, and ion exchange between water and clay minerals.

Two approaches, mathematical and graphical, are generally used to investigate hydrogeochemical evolution. The

**Table 2** Saturation indices (SI) of groundwater from the Merdja aquifer

Well	SI calcite	SI dolomite	SI gypse	SI aragonite
1	-1.43	-1.38	-1.71	-1.21
2	-1.52	-1.38	-1.59	-1.3
3	-1.41	-0.39	-1.66	-1.19
4	-1.75	-0.47	-1.46	-1.53
5	-1.12	0.49	-0.99	-0.9
6	-1.05	-0.55	-1.46	-0.83
7	-0.91	-0.22	-0.61	-0.69
8	-0.52	-0.14	-0.95	-0.3
9	-1.3	0.38	-0.87	-1.08
10	-1.05	-0.93	-1.43	-0.83
11	-1.41	-0.45	-1.84	-1.19
12	-1.76	0.45	-1.05	-1.54
13	-1.72	-0.21	-1.58	-1.5
14	-1.54	-0.86	-1.7	-1.32
15	-1.71	-0.32	-1.61	-1.49
16	-1.44	-1.1	-1.71	-1.22
17	-0.99	0.08	-1.1	-0.77
18	-1.71	-0.24	-1.44	-1.49
19	-0.99	-0.61	-1.24	-0.77
20	-1.45	-0.94	-1.47	-1.23
21	-0.68	-0.14	-1.43	-0.46
22	-1.34	-1.83	-1.58	-1.12
23	-1.38	-1.69	-1.68	-1.16
24	-1.44	0.26	-0.88	-1.22
25	-0.68	-0.29	-1.31	-0.46



**Fig. 8** Plots of saturation indices with respect to some carbonate and evaporite minerals, as computed with WATECF against total dissolved solids. *Hatched zone* indicates the saturation state

mathematical approach is often used for the calculation of saturation indices of groundwater with respect to mineral phases, thus providing some indication upon the equilibrium state between groundwater and the surrounding mineral rock assemblages. Several geochemical programs (Plummer et al. 1976; Plummer et al. 1991) have been developed for such calculations. The graphical approach describes the mineral stability fields of minerals in equilibrium with groundwater, in terms of activity ratio (on a log scale) of ions in groundwater (Plummer et al. 1976, 1991).

In the present study, saturation indices (SI) with respect to carbonate (calcite, dolomite, and aragonite) and evaporite (gypsum and anhydrite) minerals, as well as activities of soluble species (Table 2), were calculated by using the computer chemical program PHREEQC. Because all the investigated groundwaters have very low total dissolved solids, the expression of Debye and Hückel (1923) was used for the computation of activity coefficient.

Figure 8 shows the poles of SI against total dissolved solids for all investigated groundwater. In the following

discussion, we may assume that SI values falling within the range of  $\pm 0.5$  U from zero indicate the equilibrium state. All of considered groundwaters are in the state of equilibrium with respect to calcite and most of them are undersaturated with respect to dolomite; however, all samples are undersaturated with respect to aragonite (Fig. 8a–e) indicating phases undergoing dissolution especially for dolomite ( $\log K_s = -17.09$  in WATEQ)

On the other hand, groundwater samples are found to be undersaturated with respect to evaporate minerals (gypsum and anhydrite), suggesting that these evaporite mineral phases are absent in the corresponding host rock.

## Conclusions

Groundwater is unique for agriculture in the study area. However, elevated nitrate concentrations are of great concern in the groundwater of the alluvial aquifer of the Merdja plain. Agricultural practices involving synthetic

fertilizers have been identified as the main source of nitrate contamination in groundwater. Concentrations of  $\text{NO}_3^-$  higher than 50 mg/l were observed in irrigation wells located in center part of the plain, where there is heavy agricultural activity above the aquifer and crops are still irrigated using surface irrigation systems. In addition, it has been observed that denitrification is not a significant process in this shallow aquifer due to relatively high dissolved oxygen concentrations in groundwater.

Not only agricultural activities but also the mineralogical composition of the sediments in contact with groundwater determines the spatial distribution of the major ions and groundwater chemistry. Two hydrochemical facies have been identified. The change of facies is accompanied by a gradual increase in the groundwater TDS and is mainly controlled by dissolution of evaporites present in the Triassic unit. The analysis of saturation indices for calcite, dolomite, and gypsum showed that evaporites dissolution and dedolomitization (calcite precipitation and dolomite dissolution driven by gypsum dissolution) are the main hydrogeochemical processes that control groundwater chemistry.

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