

# Groundwater quality assessment in semi-arid regions using integrated approaches: the case of Grombalia aquifer (NE Tunisia)

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Abstract As many arid and semi-arid regions in the Mediterranean Basin, the Grombalia coastal aquifer (NE Tunisia) is affected by severe groundwater exploitation and contamination. Therefore, quality assessments are becoming increasingly important as the long-term protection of water resources is at stake. Multidisciplinary investigations, like the one presented in this paper, are particularly effective in identifying the different origins of mineralization within an aquifer and investigating the impact of anthropogenic activities on groundwater quality. An integrated assessment, focused on the combined use of geostatistical, geochemical and isotopic ( $\delta^{18}$ O,  $\delta^2$ H and <sup>3</sup>H) tools, was performed in the Grombalia aquifer between February and March 2014. The overall goal was to study the main processes controlling aquifer salinization, with special focus to nitrate contamination. Results indicate a persisting deterioration of water quality over the whole basin except the south-eastern zone

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juxtaposing the recharge area of the aquifer. Nitrate contents exceed the drinking water standard (50 mg/l) in 70% of groundwater samples, mainly due to the excessive use of fertilizers and urban activities. Stable isotope measurements showed the contribution of modern rainwater to aquifer recharge and proved the presence of evaporation contributing to the salinity increase. Tritium values of groundwater samples suggested two hypotheses: the existence of mixture between old and recent water or/and the existence of two recharge periods of the aquifer, pre- and post-nuclear weapons test. Principal component analysis confirmed the geochemical interpretation, highlighting that water-rock interaction evaporation effect and intensive anthropogenic activities constitute the main processes controlling the regional groundwater mineralization.

**Keywords** Groundwater · Isotopes · Geostatistics · Mineralization · Nitrate pollution

## Introduction

Groundwater is the main source of renewable freshwater for many Mediterranean countries, especially in the arid and semi-arid coastal zones of southern Europe, the Middle East and North Africa Region (Re and Zuppi 2011). In these areas, the rapid population growth associated with intensive economic activities results in a severe increase in water demand (Zghibi et al. 2013; Machiwal and Jha 2015), leading to excessive groundwater exploitation (Paniconi et al. 2001; Giordano 2009;

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Siebert et al. 2010; Van der Gun 2012). This is why water scarcity is becoming an important concern, in both urban and rural zones along the Mediterranean, where groundwater is intensively used for irrigation and domestic consumption (Edmunds 2009; GWP 2012; UNESCO-ISARM 2004; Zuppi 2008; Ouhamdouch et al. 2016). In addition to the emergence of water scarcity issues, groundwater quality degradation is also threatening the natural conditions of coastal aquifers and the associated well-being of both local populations and natural ecosystems. In this regard, the main causes of groundwater quality deterioration can be identified in aquifer salinization (often related to seawater intrusion) and pollution, generally caused by intensive anthropogenic activities (e.g. industry and agriculture) and by the lack of adequate control of sewage and waste disposal (Zuppi 2008). The combined impact of all these phenomena leads to an increase in groundwater mineralization, affecting its quality for current and future uses (Koutsoyiannis et al. 2010; Re and Zuppi 2011; Khan and Jhariya 2017). For this reason, understanding the main causes of groundwater salinization is of paramount importance in order to ensure adequate water quality protection measures and to avoid potential health and food security issues (Re et al. 2014; Zuppi 2008).

As many other zones along the Mediterranean Basin, the north-eastern part of Tunisia is characterized by dominant agricultural activities, making the Cap Bon Peninsula one of the most important agricultural district of the country. In this area, the increasing withdrawal for urban and industrial purposes, coupled to an intensive agricultural exploitation, is causing acute groundwater scarcity issues (Sebei et al. 2004; Hamza et al. 2010) and is severely threatening the quality of shallow groundwater. As a result, groundwater is generally unsuitable for domestic purposes (Ben Hamouda et al. 2010). In particular, as concerns groundwater quality, nitrate pollution is one of the main problems affecting the region, and thus a great challenge for current water management plans (Zouari et al. 2015; Re et al. 2017). In fact, although the intensive use of fertilizers has improved the regional agricultural production, its negative impacts on water quality have to be measured and assessed in order to promote new remediation measures. Based on a review of the available hydrogeochemical and hydrogeological data, the Grombalia aquifer (western part of Cap Bon Peninsula) has been chosen as priority area to assess the links of regional agricultural activities with aquifer overexploitation and salinization. Several hydrogeological and hydrochemical investigations of Grombalia coastal aquifer have been carried out during the last decennia for the crucial role of these water resources on regional development (Ben Moussa and Zouari 2011; Charfi et al. 2013; Hadj Sassi et al. 2006; Hamza et al. 2010; Sebei et al. 2004; Tlili-Zrelli et al. 2013; Gaaloul et al. 2014). The area is in fact characterized by an increase of groundwater salinity and nitrate concentrations, posing serious concerns for the local population. Nevertheless, as local population continues to exert pressure on the shallow coastal aquifer, like in many regions along the Mediterranean Basin, a more complete assessment on groundwater pollution origin is needed in order to support a more effective management of groundwater resources. Hydrogeochemical and isotopic results, coupled with a socioeconomic analysis, will be used to promote alternative science-based management strategies to ensure a more sustainable use of available water resources in the region (Re 2015; Tringali et al. 2017). In this framework, the main objectives of this study are (i) to assess groundwater quality and to identify the main geochemical processes contributing to water mineralization in the Grombalia shallow aquifer, (ii) to study the aquifer recharge and (iii) to investigate the impact of agricultural and anthropogenic activities on groundwater quality.

#### Study area

The Grombalia plain is located in north-east Tunisia, in the Cap Bon peninsula, and covers a surface of about 719  $\text{km}^2$ . It is limited by the Gulf of Tunis (N), the oriental coastal plain and Abderrahman Mountain (E), the Takelsa Syncline (NE), the Halloufa and Bouchoucha Mountains (W) and the plain of Hammamet (S) (Fig. 1). The area is characterized by a semi-arid to sub-humid Mediterranean climate with an average annual rainfall value of 512 mm/year, a mean annual temperature of 18 °C (minimum value in January and the maximum in August) and an intense potential evapotranspiration of 920 mm/year, due to the convergence of several climatic parameters (Charfi et al. 2013) like rainfall variability in time and space. The study area is characterized by both an intensive agricultural land use, with permanent (citrus, orange, olives and viticulture) and annual (vegetables, grapes and cereals) crops and industrial activities (e.g. agri-food and dairy industries), especially in the northern part



Fig. 1 Location and geological map of the Grombalia region, NE Tunisia (modified after Castany 1948)

of the plain. Urban regions characterize the city centres of Menzel Bou Zelfa, Beni Kalled, Grombalia, Bou Argoub and Soliman.

### Geology and hydrogeology

Previous studies (Castany 1948; Schoeller 1939; Ben Salem 1992) showed that Grombalia plain contains a series of marine and continental Quaternary terraces; the recent terraces are located in the north of the plain, while the old Quaternary terraces outcrop on the south. A transition of formations' lithology is shown passing from continental deposits (sands, sandstones and pebbles) toward coastal deposits in the north of the basin closed to Gulf of Tunis. Geologically, the Grombalia plain is defined as a graben-oriented NW-SE generated by two normal faults which constitute the boundaries of the study area (Ben Ayed 1993). The Hammamet fault, situated in the east of the plain, is oriented NE-SW and the Borj Cedria one, located in the west part of the basin, is oriented NNW-SSE (Fig. 1). These faults, which appeared in the Middle Miocene, have contributed to the collapse of the plain, giving rise to a rift (Ben Ayed 1993; Hadj Sassi et al. 2006). This graben is filled by Quaternary deposits, which is composed of alternating layers of permeable sand and relatively impervious marl layers forming a multilayered aquifer system. From hydrogeologic point of view, this basin presents three principal aquifers interconnected between them: the confined deep aquifer (thickness about 200 m), the confined overlying (100 m) and the phreatic unconfined aquifer (40 m) (Ennabli 1980). The upper unconfined aquifer is composed of the Quaternary continental deposits (sand, sandstones and clavey sand) at depths ranging between 15 and 40 m and overlying 15 m thick of clay substratum (Ben Moussa and Zouari 2011). It is topped with a layer of vegetal cover with a thickness of about 10 m (Fig. 2). The aquifer horizontal transmissivity ranges between  $25 \times 10^{-4}$  and  $2 \times 10^{-2}$  m<sup>2</sup>/s, and the storage coefficient is about  $5.5 \times 10^{-3}$  (Tlili-Zrelli et al.

**Fig. 2** Hydrogeological cross section of Grombalia Basin (modified after Charfi 2015)



2013). The total exploitation has increased from 89.7  $Mm^3$  in 1990 to 106  $Mm^3$  in 2015, while the renewable resources are estimated to 51  $Mm^3$ /year which led to an overexploitation state of Grombalia shallow aquifer of about 208% (DGRE 1990– 2015). In order to improve groundwater quality and quantity, recently the injection of surface water from Medjerda canal and the implementation of infiltration basins are adopted as artificial recharge techniques.

The deep layer is housed in Quaternary marine sandstone with an average thickness of 35 m tapped by many boreholes at depths varying from 90 to 110 m. These two aquifers constitute the main reservoir of the Grombalia hydrogeological system. Both aquifers are separated by sandy clay deposits with a thickness ranging between 30 m (SW) and 50 m (NE).

# Piezometric study

The piezometric map of Grombalia shallow aquifer (Fig. 3a) was established based on the water-level depth measurement of 29 wells realized by the Regional Commissariat for Agricultural Development (CRDA) of Nabeul in 2014. The map indicates that the main groundwater flow direction is SE-NW, i.e. from the recharge area located in the south, especially in Bou Argoub region and the foothills of Abderrahman's Mountain, toward the gulf of Tunis and Sebkha el Melah as the natural discharge areas (Ennabli 1980). The piezometric map shows that groundwater hydraulic head decreases progressively toward the sea, from 60 m in the

south of Beni Kalled, to 5 m in Soliman region. The comparison between the piezometric level in 1968 and in 2014 (Fig. 3b) clearly shows a general decline of the groundwater level with about 10 m over a period of 47 years in Grombalia Basin. Thus, the average decline is about 21 cm/year which affected almost the whole region, although the main flow direction has not changed. This lowering of the groundwater level is in relation with the decrease in average rainfall over the whole region and the overexploitation of groundwater resources. The general shape of the piezometric curves in the north-eastern and north-western part of the plain was regular (in 1968) showing a flat aquifer. However, they have currently become concave in upstream basin indicating a shift to a radial aquifer thread diverging essentially fuelled by Wadis Elbey and its effluents which can be due to the changes in land use, overabstraction and the deviation of the flow direction of some wadis (i.e. ephemeral rivers) on the surface over the years.

# Materials and methods

Groundwater sampling and analyses

Between February and March 2014, a total of 27 groundwater samples were collected in the Grombalia upper aquifer from wells and boreholes (Table 1). All groundwater samples were analysed for chemical and isotopic composition at the Laboratory of Radio-





Fig. 3 Piezometric map of the Grombalia shallow aquifer (a) in 2014 and (b) in 1968 (according to Castany 1968)

No.	T (°C)	Hd	EC (µS/cm)	Cl <sup>-</sup> (mg/l)	NO <sub>3</sub> <sup>-</sup> (mg/l)	$SO_4^{2-}$ (mg/l)	HCO <sub>3</sub> <sup>-</sup> (mg/l)	Na <sup>+</sup> (mg/l)	K <sup>+</sup> (mg/l)	Mg <sup>2+</sup> (mg/l)	Ca <sup>2+</sup> (mg/l)	TDS (mg/l)
-	10.0	90 <del>9</del>	0100	1020 A	10.5	707	252 0	1102 7	10.0	5 COC	ר פרר	6750
- 0	10.0	0.70	0016	4.702.2	0.04 0.02 c	0.461	0.000	1195.6	10.0	C.262	7.011	00001
7	21.3	1.37	2650	502.8	127.8	264.1	231.8	290.8	21.6	63.9	189.3	1692
ŝ	20.3	7.30	5720	1300.6	203.5	509.7	286.7	734.7	14.7	130.4	359.1	3539
4	18.4	7.00	5290	1450.0	419.6	723.1	292.8	585.3	28.8	147.8	610.0	4258
5	16.5	7.39	4490	815.6	465.8	554.5	329.4	422.7	35.6	93.6	395.6	3113
9	15.7	7.35	4690	893.4	85.1	610.4	414.8	530.0	0.0	86.5	405.0	3025
7	19.8	7.06	3530	661.2	155.3	296.3	414.8	298.2	17.0	111.8	302.0	2257
8	20.3	7.04	5030	1261.0	17.5	548.0	396.5	639.8	40.3	163.5	341.4	3408
6	17.5	7.27	3730	688.5	84.6	572.7	335.5	417.1	11.1	86.5	320.0	2516
10	18.2	7.13	2650	520.1	163.4	169.2	317.2	202.6	18.3	51.8	302.0	1745
11	16.6	7.42	2220	415.8	0.0	366.6	164.7	274.3	13.9	50.6	146.2	1432
12	18.7	6.92	3120	418.9	133.1	397.5	457.5	264.4	39.8	61.8	302.5	2075
13	16.6	7.20	4160	834.7	162.5	513.1	378.2	463.3	0.0	95.0	369.3	2816
14	18.2	6.92	5350	1162.8	514.7	583.6	292.8	498.4	14.6	90.2	677.4	3834
15	17.9	7.09	3860	816.2	281.8	362.4	256.2	285.5	17.4	74.3	382.9	2477
16	18.1	7.16	3680	812.9	288.3	270.5	292.8	251.6	2.5	83.0	480.0	2482
17	20.0	7.06	4400	1171.3	3.0	635.7	469.7	512.5	16.5	186.6	422.9	3418
18	17.5	7.20	3440	654.7	67.0	431.2	341.6	312.0	7.9	72.3	345.0	2232
19	18.8	7.23	2390	408.8	94.2	252.9	347.7	197.9	16.8	65.5	202.7	1587
20	17.2	7.27	2700	485.7	157.4	268.0	298.9	217.8	28.0	55.0	290.6	1801
21	20.4	7.00	3410	733.1	132.7	345.0	292.8	351.0	20.0	90.4	198.1	2163
22	17.9	7.61	3120	606.4	87.8	330.9	292.8	247.4	10.6	95.9	258.5	1930
23	17.7	7.80	1039	112.4	11.1	145.3	231.8	111.1	8.5	26.1	69.0	715
24	19.4	7.16	3019	643.6	12.2	350.1	323.3	321.0	11.2	90.5	244.6	1997
25	18.3	7.09	2770	451.7	22.4	398.1	481.9	325.1	19.1	65.5	231.8	1996
26	17.6	7.23	4390	1009.6	112.6	407.2	317.2	376.1	11.2	127.7	406.5	2768
27	16.4	7.45	3550	687.6	17.7	570.2	353.8	330.6	12.7	130.7	304.5	2408
Min.	15.7	6.92	1039	112.4	0.0	145.3	164.7	111.1	0.0	26.1	69.0	715
Max.	21.3	7.80	9180	2932.4	514.7	759.6	481.9	1193.7	40.3	292.3	775.2	6358
Mean	18.3	7.21	3836	831.5	143.0	431.0	332.1	394.7	16.6	9.66	345.1	2594
Std.dev.	1.4	0.20	1517	525.0	140.7	162.6	74.3	216.2	10.5	53.1	155.1	1096
oN N	Hardness (	ma/l)	λ <sup>18</sup> Ο (%, ver	CMOWS SHIP	5 <sup>2</sup> Н (%, уменис	H <sub>E</sub> UMOMS	(TII) SI anhvd	rite SI arado	nite SI calc	vite SI dolomi	ite SI avmsur	SI halite
.041		(1,8)		( M O MIC ene	eneral and II a						med 12 m	
1	3156		-5.4		- 31.3	1.5	96 - 0.67	0.25	0.40	0.65	-0.43	-4.17
2	739		-5.1		-31.9	2.'	12 - 1.30	0.15	0.30	0.42	-1.07	-5.47
3	1441		-5.2		-31.4	2	-0.95	0.31	0.46	0.77	-0.72	-4.7
4	2142		-4.5		-28.2	1.8	30 - 0.66	0.18	0.33	0.32	-0.42	-4.76
5	1379		-4.1		- 25.7	2.5	7 -0.83	0.47	0.62	0.85	-0.59	-5.12
												-

Table 1 (	continued)									
No.	Hardness (mg/l)	$\delta^{18}$ O (% versus SMOW)	δ <sup>2</sup> H (%o versus SMOW)	<sup>3</sup> H (TU)	SI anhydrite	SI aragonite	SI calcite	SI dolomite	SI gypsum	SI halite
6	1373	-4.0	- 24.0	2.56	- 0.79	0.52	0.67	0.89	-0.54	-4.98
7	1221	- 5.0	- 29.8	1.6	-1.16	0.22	0.37	0.60	-0.92	-5.36
8	1535	-4.9	- 30.2	1.31	- 0.95	0.17	0.32	0.61	-0.72	-4.77
6	1160	-3.7	- 24.5	2.34	-0.87	0.30	0.45	0.57	-0.63	-5.19
10	971	-4.3	- 29.2	1.78	- 1.32	0.20	0.35	0.20	-1.08	-5.61
11	576	-3.5	- 20.8	4.13	-1.23	-0.13	0.02	-0.18	-0.99	-5.56
12	1013	-4.0	- 26.9	5.59	-0.99	0.12	0.27	0.11	-0.75	-5.59
13	1319	- 3.9	- 26.6	2.59	-0.88	0.32	0.47	0.59	-0.64	-5.07
14	2069	- 4.3	- 26.2	3.76	-0.68	0.17	0.32	0.02	-0.44	-4.92
15	1267	-4.5	- 27.3	1.22	-0.98	0.11	0.26	0.06	-0.74	-5.28
16	1546	-5.1	- 30.2	2.69	-1.04	0.33	0.48	0.47	-0.80	-5.34
17	1835	-4.5	- 29.2	0.86	-0.82	0.34	0.49	0.91	-0.59	-4.90
18	1164	-4.3	- 30.2	5.21	-0.94	0.29	0.44	0.46	-0.69	-5.33
19	780	-4.9	- 32.0	1.11	- 1.28	0.19	0.33	0.45	-1.04	-5.72
20	956	-4.9	- 29.4	2.35	- 1.14	0.27	0.42	0.37	-0.90	-5.60
21	872	-4.7	- 27.3	2.37	-1.22	-0.15	0.00	-0.05	-0.99	- 5.24
22	1046	-4.4	- 28.3	0.57	-1.14	0.54	0.69	1.20	-0.89	- 5.46
23	281	- 5.4	-37.1	I	-1.77	0.20	0.35	0.53	- 1.53	-6.48
24	686	I	Ι	0.00	-1.14	0.13	0.28	0.40	-0.90	-5.33
25	852	-4.4	- 26.8	2.43	-1.09	0.19	0.34	0.40	-0.84	-5.47
26	1548	-4.6	- 28.5	2.41	-0.96	0.33	0.48	0.72	-0.72	-5.08
27	1306	-4.8	- 26.3	1.49	-0.91	0.46	0.61	1.09	-0.66	-5.29
Min.	281	-5.4	-37.1	0.00	-1.77	-0.15	0.00	-0.18	- 1.53	-6.48
Max.	3156	-3.5	- 20.8	5.59	-0.66	0.54	0.69	1.20	-0.42	-4.17
Mean	1279	-4.5	- 28.4	2.28	-1.02	0.24	0.39	0.50	-0.79	-5.25
Std.dev.	564.2	0.5	3.2	1.28	0.24	0.16	0.16	0.34	0.24	0.43

Analyses and Environment (LRAE) in the National School of Engineers of Sfax (Tunisia). The measurements of temperature (T), pH and electrical conductivity (EC) were performed on-site for each well; major elements (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Ca<sup>2+</sup>) were analysed by high-performance liquid chromatography (HPLC-Waters) equipped with IC-Pak TM CM/D columns for cations, using EDTA and nitric acid as eluent, and on a Metrohm chromatograph equipped with CI SUPER-SEP columns for anions, using phthalic acid and acetonitrile as eluent. The overall detection limit for ions was 0.04 mg/l. Alkalinity was analysed in the laboratory by titration using 0.1 N HCl acid. The measurement of total dissolved solids (TDS) was performed by evaporating 100 ml of groundwater sample at 105 °C during 24 h. The ionic balance for all samples was within  $\pm$  5%. The spatial distribution maps of the salinity and nitrate contents were carried out using the software package of Arc GIS (Ver. 9.3). Saturation indices for halite, anhydrite, gypsum and carbonates were calculated using the Diagrammes software (Hydrogeological Laboratory of Avignon). Stable isotope analyses ( $\delta^{18}$ O and  $\delta^{2}$ H) of the water samples were measured using the laser absorption spectrometer, LGR DLT 100 (Penna et al. 2010), and the results are reported in delta value expressed in %o versus SMOW (standard mean ocean water). The uncertainly of stable isotope measurements is  $\pm 0.1\%$  for  $\delta^{18}O$  and  $\pm 1\%$  for  $\delta^2$ H. Samples were analysed for tritium contents using electrolytic enrichment and liquid scintillation counter (Taylor 1977). Tritium content is expressed in tritium units (TU) with a precision of measurement equal to  $\pm 0.3$  TU.

#### Geostatistical and statistical investigation

Spatial distribution maps were performed based on geostatistical approach using the kriging technique for data modelling. Ordinary kriging method was applied in this work as surface estimator to better identify the contaminated areas and understand the spatial and temporal variability of nitrate contents and its relation with agricultural and domestic activities' growth. The semi-variogram is the basic geostatistic technique. It is represented by two axes: the *x*-axis indicates the distance separating the pair of points that most widely varied in the input data, and the *y*-axis represents the semi-variance  $\gamma(h)$ . A variogram is characterized by the following parameters (Baillargeon 2005): (i) the sill which

represent the value of the variogram for the distance equal to the range, (ii) the range which means distance where two cases are different with covariance is equal to zero and (iii) the nugget effect representing the behaviour of the variogram's origin reflecting the degree of spatial regularity of the regionalized variable. If the variogram has a nugget effect, this indicates a partial lack of correlation between the values found in two close sites. The semi-variogram ( $\gamma(h)$ ) is defined as half the average quadratic difference between two points separated by the distance vector (*h*) (Journel and Huijbregts 1978) according to the following formula (1):

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(xi) - Z(xi + h)]^2$$
(1)

where N(h) represents the total number of the variable pairs separated by this distance and z(x) is the value of the variable. For the purpose of the present study, modelling of spatial distribution of nitrate concentrations and the calculation of experimental variograms were performed using geostatistical tools integrated into Surfer 9 software (Golden Software Inc., CO, USA).

Multivariate statistical analysis was applied on the hydrochemical and isotopic data to identify the different mechanisms that control groundwater mineralization. Principal component analysis (PCA) aims to summarize the maximum possible information by losing as little as possible of variables in order to facilitate the interpretation of a large number of initial data and to give more meaning to the reduced data (Chatfield and Collins 1980; Kihumba et al. 2016). Statistical data treatment was performed using the statistical software SPSS Statistics for Windows version 17.0 (SPSS, Inc., Chicago, USA, 2008).

## **Results and discussion**

## Aquifer recharge and mineralization origin

The physico-chemical data of the analysed groundwater samples (Table 1) show a relatively wide range of temperature values, from 15.7 to 21.3 °C (average 18.3 °C). This variation can be related to the different water table depth and to the influence of the atmospheric temperature. The pH values range from 6.92 to 7.80 with an average of 7.21 indicating that most of samples are neutral. The average electrical conductivity is  $3836 \ \mu\text{S}/\text{cm}$  varying within a wide range of values from  $1039 \ \mu\text{S}/\text{cm}$  in well 23, located in the south-western of the plain, to  $9180 \ \mu\text{S}/\text{cm}$  in well 1, located near to the sea shore.

The chemical composition of analysed samples is presented in Table 1 and plotted on the Piper diagram (Piper 1944) to specify the different groundwater types of Grombalia shallow aquifer. When representing data on such diagram, nitrate concentrations were also taken into account, since they are not negligible due to their high values (Table 1). The triangle of cations shows that the majority of samples belong to the mixed pole whereas some groundwater samples indicate the slight dominance of calcium and magnesium. Sample 16 has the highest percentage of calcium, and this can be due to cation exchange process. The triangle of anions shows the predominance of chloride and nitrate for the majority of samples except for sample nos. 23 and 25 which belong to the mixed pole. The chemical data plotted in this diagram reveals the dominance of the Ca-Mg-Cl/ NO<sub>3</sub> water type (Fig. 4).

In the study region, the salinity has a large variability, as demonstrated by the total dissolved solids (TDS) ranging from 715 mg/l (well 23) to 6358 mg/l (well 1), with an average of 2594 mg/l. This indicates that most samples (96%) are not adequate for drinking use, having TDS concentrations exceeding 1000 mg/l (WHO 2011).

**Fig. 4** Piper diagram of the Grombalia shallow aquifer

The salinity distribution map (Fig. 5) shows that lower TDS values are located in the south-eastern and southwestern zones of the Grombalia Basin, due to the possible dilution phenomenon resulting from aquifer recharge in the basin borders. On the other hand, higher TDS, characterizing some samples in the centre of the plain, can be associated to the abundance of evaporate deposits and the presence of intensive agriculture activities. The highest mineralization occurs in the north of the basin (wells 1, 3, 4, 5, 8) near the salt deposits (sebkha) and the Mediterranean Sea shore. In addition, for agricultural use, salinity has an adverse effect on plant growth while sodium affects soil physical properties such as infiltration (Subramani et al. 2005). The distribution of salinity levels partially conforms to the principal groundwater flow direction and may be controlled by the residence time within the aquifer.

Table 1 shows the variability of major anion and cation concentration in the collected samples. Accordingly, this aquifer displays higher concentrations in dissolved ions, with the highest variations observed for chloride, sulphate, nitrate, calcium, and sodium, while the variations of bicarbonate, potassium, and magnesium are rather smaller. Chloride is the predominant anion in the Grombalia aquifer. The highest Cl<sup>-</sup> concentration (2932.4 mg/l) is recorded in the north of the aquifer near the coastal area suggesting the potential





Fig. 5 Sampling network and salinity distribution map. Numbers in the figure correspond to the sampling sites indicated in Table 1

occurrence of anthropogenic inputs of chloride and the effects of marine aerosol spray. The nitrate contents are generally moderate to high (up to 514.7 mg/l), especially for well nos. 4, 5, 14, and 16, and with concentrations exceeding the WHO drinking limit (50 mg/l; WHO 2011) in 70% of the wells. The measured calcium contents show high variability with a mean of 345.1 mg/l. Sulphates show moderate levels, ranging from 145.3 mg/l (well 23) to 759.6 mg/l (well 1). In this case, associated with a high content in calcium, sulphate inputs may be linked to sulphate mineral dissolution. Bicarbonate values range from 164.7 mg/l (well 11) to 481.9 mg/l (well 25). A higher variability is observed for the whole basin concerning sodium contents which vary between 111.1 mg/l (well 23) and 1193.7 mg/l (well 1). Generally, potassium and magnesium contents in the analysed water samples are very low showing mainly homogenous values for the whole aquifer.

The diagram of Na<sup>+</sup> versus Cl<sup>-</sup> (Fig. 6a) shows high correlation with some points located around the dissolution line of halite, indicating a possible common origin

of these two elements coming from halite dissolution, as explained by the reaction:  $(NaCl + 2H_2O \rightarrow Na^+ +$  $Cl^{-} + 2H_2O$ ). The dissolution process can also be highlighted, by both the under-saturation state (SI < 0) for all samples, with respect to halite (Table 1), and the proportional parabolic correlation between the saturation indices (SI) and the sum of Na and Cl (Fig. 7a). However, several points are situated under the 1:1 halite dissolution line with an excess of Cl indicating various origins of chloride. For some samples, halite is highly under-saturated. Hence, it may not be the only source of Na and Cl. Sodium and chloride likely originated also from surface contamination sources or saline sources (*Sebkha*). The diagram of  $Ca^{2+}$  versus  $SO_4^{2-}$  (Fig. 6b) shows a calcium excess for most of the samples, whereas some points (well nos. 11, 23, 21, 25 and 27) indicate a relative positive correlation between calcium and sulphate ( $R^2 = 0.522$ ), that may highlight the same origin of these two elements related to the dissolution of sulphate minerals (gypsum and anhydrite). The negative saturation indices (Fig. 7b, c) of all groundwater samples



Fig. 6 Relationship between major elements. a Na versus Cl. b Ca versus SO<sub>4</sub>. c Ca versus HCO<sub>3</sub>. d (Na + K) - Cl versus  $(Ca + Mg) - (SO_4 + HCO_3)$ 

indicate under-saturation state with respect to the gypsum and anhydrite confirmed as well as the dissolution process of sulphate minerals. Therefore, the excess of calcium and the sodium deficiency can be attributed to cation exchange reaction that significantly affects groundwater chemical composition, by which the Na<sup>+</sup> cations are adsorbed by clay minerals on their surface against the release of Ca<sup>2+</sup> according to the reaction:  $(Ca-clay(s) + 2Na^+ \rightarrow Na_2-clay(s) + Ca^{2+})$ . The cation exchange process is confirmed by the relation between  $[(Ca^{2+} + Mg^{2+}) - (HCO_3^{-} + SO_4^{-2-})]$  and  $[Na^+ + K^+ -$ Cl<sup>-</sup>] examined in Fig. 6d (Garcia et al. 2001). The  $[(Ca + Mg) - (SO_4 + HCO_3)]$  represents the amount of calcium and magnesium gained or lost relative to that provided by the dissolution of gypsum, dolomite, and calcite, whereas [Na+K-Cl] values represent the amount of sodium and potassium gained or lost relative to that provided by the dissolution of halite (Fisher and Mullican 1997). These exchanges are confirmed by the sample position along a line with slope equal to -1. In the case of the absence of these exchange reactions, points should be placed close to the origin point (Abid et al. 2009; McLean et al. 2000). Figure 6d shows that majority of groundwater samples in the Grombalia Basin define a straight line ( $R^2 = 0.927$ ) with a slope of – 1.27, indicating that cation exchange reactions represent a principal contributor to groundwater mineralization. Also, the use of Ca(NO<sub>3</sub>)<sub>2</sub> fertilizers increases the calcium content and contaminates the groundwater by the irrigation return flow (Stigter et al. 2006).

The diagram of  $Ca^{2+}$  versus  $HCO_3^-$  (Fig. 6c) shows a poor correlation between these two elements, indicating the inability of groundwater to dissolve calcite and dolomite due to the oversaturation (SI > 0) and equilibrium states (SI = 0) with respect to these minerals (Fig. 7e–f). Thus, Ca appears to be mainly derived from either origin like the dissolution of evaporites (anhydrite and gypsum), cation exchange process and fertilizers.

The stable isotope ratios of the water molecule range between -5.4 and -3.5% versus SMOW (mean of -4.5) for  $\delta^{18}$ O and between -37.1 and -20.8% versus SMOW (mean of -28.4) for  $\delta^{2}$ H. Figure 8 highlights the presence of two distinct



Fig. 7 Plots of a (Na + Cl)/SI halite, b  $(Ca + SO_4)/SI$  gypsum, c  $(Ca + SO_4)/SI$  anhydrite, d  $(Ca + CO_3)/SI$  calcite, e  $(Ca + Mg + HCO_3)/SI$  dolomite and f  $(Ca + CO_3)/SI$  aragonite

groups. The first one (G1) with the samples falling between the Global Meteoric Water Line (GMWL:  $\delta^2 H = 8.17 \ \delta^{18}O + 10.35$ ; Rozanski et al. 1993) and the Local Meteoric Water Line of Tunis-Carthage (LMWL:  $\delta^2 H = 8 \ \delta^{18}O + 12.4$ ; Zouari et al. 1985) points out the strong contribution of direct rainwater infiltration to aquifer recharge, especially for points located near the hydrographic network (*wadis*), hence confirming the rapid and recent recharge. On the other hand, the second group (G2) is characterized by samples with more enriched isotope compositions, placed below both the GMWL and the LMWL. This group corresponds to the samples dominated by an evaporation effect, according to the equation:  $\delta^2 H = 5.3 \ \delta^{18}O - 4.3$ , indicating either the slow infiltration of rainwater due to low permeable soil and/or the return flow of evaporated irrigation water.

The diagram of Cl<sup>-</sup> versus  $\delta^{18}$ O (Fig. 9) confirms the presence of two main processes contributing to the



**Fig. 8** Stable isotope composition of groundwater samples in the Grombalia Basin. Blue line corresponds to Global Meteoric Water Line (GMWL:  $\delta^2 H = 8.17 \ \delta^{18}O + 10.35$ ; Rozanski et al. 1993); red line corresponds to Local Meteoric Water Line of Tunis-Carthage (LMWL:  $\delta^2 H = 8 \ \delta^{18}O + 12.4$ ; Zouari et al. 1985), and dashed black line represents the evaporation affect

mineralization of the shallow Grombalia aquifer: (i) dissolution of evaporative rocks, dominated by the previously described water-rock interactions, and (ii) evaporation. In fact, some samples show an isotopic enrichment, designated by the dashed black arrow in Fig. 9, confirming that evaporation process contributes to groundwater mineralization.

Tritium (<sup>3</sup>H) contents in groundwater provide an indication of young groundwater ages (Dulinski et al. 2003). Its short half-life (about 12.4 years) allows it to be used as a good tool to identify recent (< 50 years) water recharge (Mann et al. 1982). It depends mainly on the initial atmospheric concentration when recharge is started and the radioactive



Fig. 9 Plot of Cl<sup>-</sup> versus  $\delta^{18}$ O; dashed black arrow corresponds to trend of isotopic enrichment

decay during infiltration from surface to saturated zone (Maduabuchi et al. 2006). The tritium activities for groundwater samples varies between 0 (well 24) and 5.59 (well 12) TU with an average of 2.28 TU. Considering tritium half-life and the tritium contents characterizing the precipitation in Tunisia during the nuclear tests in the middle of the last century, the <sup>3</sup>H contents above 2.0 TU likely indicate post-nuclear water recharge during the last 50 years or at least that some components of water have been recharged in this period. In fact, high tritium contents, which characterize the southeastern part of Grombalia Basin (i.e. the recharge area), can be attributed to recent rainfall infiltration. Waters with tritium activities below 2 TU could be explained as the pre-nuclear recharge, before the thermonuclear tests in 1950s and 1960s or the existence of mixture between recent and old waters. As it is shown on <sup>3</sup>H versus  $\delta^{18}$ O diagram (Fig. 10), tritium contents in most of analysed groundwater exceed 0.65 TU except for wells No. 22 and 24. The presence of detectable activities of tritium in groundwater highlights the modern infiltration of rainwater in this aquifer (Clark and Fritz 1997). In fact, the recent recharge signature is significant in most of the groundwater samples characterized by an enriched of  $\delta^{18}$ O isotopic composition and high <sup>3</sup>H activities. Samples with highest tritium contents (no. 11, 12, 14, and 18) indicate the direct and rapid rainwater infiltration, whereas the other samples



Fig. 10 Relation between  $\delta^{18}$ O and  $^{3}$ H in groundwater samples of Grombalia Basin

(except well nos. 22 and 24) reflect slow and/or indirect water infiltration.

#### Evaluation of water quality

Groundwater quality assessment is an important issue in hydrochemistry. Variation of water quality is a function of physical parameters and chemical composition that are greatly influenced by the geological nature of the reservoir and by anthropogenic activities (Subramani et al. 2005). Water hardness is a commonly known aspect of water quality, being a measure of the concentrations of magnesium and calcium present in water. According to World Health Organization (WHO 2011), the standard hardness level is 200 mg/l. As concerns the samples collected in the Grombalia shallow aquifer, hardness is quite high and ranging from 281 to 3156 mg/l (Table 1). These values indicate that water flowing through aquifer formations dissolves Ca and Mg minerals hence making water harder along the flow paths. In addition, excessive use of Ca(NO<sub>3</sub>)<sub>2</sub> and MgSO<sub>4</sub> fertilizers may increase water hardness highlighting the indirect contribution of synthetic fertilizers, inducing an acidic perturbation of the solution which is buffered by carbonate dissolution and leading to an increase in water hardness (Spruill et al. 2002). According to these high levels, the consumption of this water can have negative consequence for human health.

Furthermore, the majority of samples collected in the shallow aquifer show high nitrate concentrations, and about 70% of the total exceeds the statutory limit for drinking water 50 mg/l (WHO 2011). Concentrations range from 0 mg/l (well 11) to 514.7 mg/l (well 14) with an average value of 143 mg/l. Figure 11 shows that the highest concentrations are found in Beni Kalled, Menzel Bou Zelfa, and Soliman regions where agricultural activities (especially irrigated agriculture) are dominant and where the groundwater static levels are close to the surface (water table levels < 7 m), increasing the potential for contamination by the return flow of irrigation water. Indeed, this highlights the strong link between nitrate contamination and the intensive use of fertilizers, sometimes associated to the irrigation with treated wastewater, like in Soliman region, and industrial activities (e.g. agri-food and dairy industries) (Ben Moussa and Zouari 2011; Re et al. 2017). The presence of these high nitrate concentrations can be harmful for human health (Suthar et al. 2009) potentially resulting in stomach cancer for adults and methemoglobinemia in infants (Spalding and Exner 1993). On the other hand, moderate  $NO_3^-$  contents are found in the centre of the study area, and relatively low nitrate concentrations characterize Grombalia bare soils. The lower nitrate contents for some samples can be explained by either the dilution phenomenon due to freshwater infiltration or denitrification process. As Grombalia is one of the most important agricultural region in the north of Tunisia, the local nitrate contamination is therefore explained by both the intensive agriculture (i.e. excessive use of synthetic fertilizers) and domestic activities (i.e. septic system effluents and manure) which lead to increase nitrate leaching (Re et al. 2017).

Spatial and temporal variation of nitrate contents in Grombalia shallow aquifer was investigated using geostatistic tools. Nitrate distribution maps were elaborated using the cubic model as the most fitting mathematical model to the experimental variograms for both 2005 and 2014 years. The variogram of 2014 is defined by the following parameters: (i) the sill which is equal to 18,000 and where the covariance becomes zero, (ii) the range which is equal to 8400 m representing the correlation distance between two points and (iii) the nugget effect equal to zero indicating the absence of discontinuity at the origin and reflecting the local regularity of the distribution of nitrate concentrations. In 2005, the corresponding variogram is defined by the following characteristics: (i) the sill is equal to 7800, (ii) the range is about 8500 m which is close to the obtained value of 2014 and (iii) the nugget effect equals to 2000. The large value of nugget reflects the presence of a discontinuity at the origin indicating that nitrate distribution in 2005 is more irregular than in 2014.

The spatial distribution of nitrate in 2014, using ordinary kriging method (Fig. 12a), reveals that high nitrate values increased from south to north of the plain (from the recharge zone to discharge area) characterizing a SE-NW nitrate flow direction which is similar to the principal flow direction of the aquifer.

The comparison of nitrate contamination state from 2005 to 2014 (Fig. 12) reveals a remarkable reduction in nitrate levels over time, especially in the centre of the plain (urban region), and an increase of nitrate concentrations in the north-east and north parts (agricultural regions). In 2014, nitrate contents in the centre of the basin are below 20 mg/l, whereas in 2005 (Fig. 12b), the same area was characterized by a peak of nitrate pollution (up to 400 mg/l). This decrease is concordant with the salinity decline



Fig. 11 Land use map and distribution of nitrate concentrations (according to Chenini et al. 2015; CRDA 2016)

resulting from the use of river water (*wadis*) for irrigation and artificial recharge (Tlili-Zrelli et al. 2013). It could be also due to the occurrence of denitrification process resulting in a depletion of nitrate content (Boettcher et al. 1990; Mengis et al. 1999; Yuan et al. 2012; Charfi et al. 2013; Selek and Yetis 2017). Thus, shallow groundwater quality changes over time and space in Grombalia Basin, mainly due to soil occupation, aquifer recharge and pollutant transfer flow's rate. This investigation highlights also the need to set and maintain groundwater quality monitoring network to support the implementation of effective management strategies in the long run, especially in zones where shallow aquifers represent the main source of water supply for the local population, as in the case of arid and semi-arid regions.

# Statistical data treatment

The Pearson's matrix (Table 2), showing the correlation factors between 11 variables (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, TDS,  $\delta^{18}$ O,  $\delta^{2}$ H, EC and hardness), indicates that (i) the high correlation ( $R^2 > 0.8$ ) registered between Cl<sup>-</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and TDS reflects the significant contribution of these elements to the acquisition of water mineralization; (ii) the high correlation between Na<sup>+</sup> and Cl<sup>-</sup> ( $R^2 = 0.95$  and p < 0.05)

Fig. 12 Spatial distribution of nitrate using ordinary kriging as a method of interpolation **a** in 2014 and **b** in 2005



indicates that the dissolution of halite is an important process of mineralization; (iii) the positive correlation between Ca<sup>2+</sup> and NO<sub>3</sub><sup>-</sup> ( $R^2 = 0.50$  and p < 0.05) shows the effect of nitrogen fertilizers; and (iv) the high correlation between Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ( $R^2 = 0.72$  and p < 0.05) shows the dissolution of sulphate minerals.

Hydrochemical and isotopic data were analysed and interpreted using the principal component analysis (PCA) as an extraction method helpful for groundwater quality evaluation. Three principal components (with eigenvalues > 1) were selected to explain 94.515% of the total variance (65.278% for F1, 18.841% for F2 and 10.396% for F3: Table 3) which conform to Kaiser-Meyer-Olkin (KMO) and Bartlett's test conditions. The KMO measure of sampling adequacy is about 0.749, and Bartlett's test of sphericity is equal to zero. These two parameters ensure that the necessary conditions of the PCA are satisfied.

According to the obtained results, the first factor (F1) represents groundwater salinity due to the highly positive loading of TDS, EC, hardness, Na<sup>+</sup>, Cl<sup>-</sup>, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2</sup> and Mg<sup>2+</sup> (Fig. 13). This factor indicates that the main

		Cl_	$NO_3^-$	${{\rm SO_4}^2}$	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	TDS	$\delta^{18}O$	$\delta^2 H$	EC	Hardness
Correlation index $(R^2)$	Cl	1				:						
	$NO_3^-$	0.14	1									
	$\mathrm{SO_4}^{2-}$	0.74	0.17	1								
	Na <sup>+</sup>	0.95	0.05	0.80	1							
	Mg <sup>2+</sup>	0.92	-0.08	0.74	0.88	1						
	Ca <sup>2+</sup>	0.84	0.50	0.72	0.73	0.69	1					
	TDS	0.97	0.28	0.84	0.94	0.89	0.90	1				
	$\delta^{18}O$	-0.28	0.09	0.20	-0.19	-0.32	-0.07	-0.15	1			
	$\delta^2 H$	-0.06	0.14	0.36	0.01	- 0.09	0.09	0.06	0.85	1		
	EC	0.97	0.24	0.80	0.95	0.88	0.87	0.98	-0.17	0.05	1	
	Hardness	0.94	0.31	0.78	0.85	0.87	0.96	0.97	-0.17	0.03	0.94	1

**Table 2** Pearson's correlation matrix of chemical and isotopic parameters; values marked in italics are significant (with significance level, p < 0.05)

geochemical process affecting groundwater quality is defined by water-rock interactions such as dissolution of evaporates (gypsum, anhydrite and halite) and cation exchange process. High positive loadings for  $\delta^{18}$ O and  $\delta^{2}$ H designated the second factor as the evaporation component (F2) and high positive loadings for NO<sub>3</sub><sup>-</sup> defined the third factor as the nitrate pollution factor (F3). The obtained results of the PCA support the evidences of hydrochemical and isotopic analyses relative to the identification of the main processes contributing

**Table 3**Loadings of 11 variables on three significant factors (F1,F2 and F3) and total variance explained; values marked in italicsare significant ( with factor > 0.5)

	F1	F2	F3
TDS	0.998	0.023	0.027
EC	0.985	-0.002	-0.002
Hardness	0.975	0.004	0.110
Cl <sup>-</sup>	0.974	-0.142	- 0.063
Na <sup>+</sup>	0.940	-0.071	-0.202
Mg <sup>2+</sup>	0.905	-0.218	-0.271
Ca <sup>2+</sup>	0.902	0.132	0.317
$\mathrm{SO_4}^{2-}$	0.843	0.352	-0.193
$\delta^2 H$	0.045	0.938	-0.195
$\delta^{18}O$	-0.169	0.936	-0.171
NO <sub>3</sub> <sup>-</sup>	0.246	0.318	0.899
Eigenvalues	7.181	2.072	1.144
% of variance	65.278	18.841	10.396
Cumulative %	65.278	84.119	94.515

to groundwater salinization. Water-rock interactions, evaporation and nitrate pollution are the main mechanisms governing groundwater chemistry in the Grombalia shallow aquifer.

The projection of all samples according to their factor scores (Fig. 14) also confirms geochemical processes. The most mineralized groundwater samples (quadrant I, Fig. 14a, b) highlight the contribution of water-rock interactions and mineral dissolution processes to the increase of water salinity. These same samples (nos. 1, 8, 17 and 26) are located on the negative sides of F2 and F3 axes (quadrant IV, Fig. 14c) and characterizing the most isotopically depleted samples. This indicates the absence of evaporation process due to the low interaction with the atmosphere and confirms the occurrence of denitrification process. This phenomenon is responsible for the biological transformation of NO<sub>3</sub><sup>--</sup> to N<sub>2</sub> causing the decrease of nitrate concentration in groundwater.

In the plot of F1 salinization versus F3 nitrate pollution (Fig. 14b), different groups can be distinguished. Samples with high scores of F3 (II and III quadrants, Fig. 14b) highlight the occurrence of nitrate pollution caused by nitrogen fertilizers leaching for samples which are located in the agricultural regions (nos. 4, 5 and 14), and from septic tanks and manure contamination for sample nos. 2, 3, 15, 16 and 26 which are situated in the urban regions. These results confirm the previous findings by Re et al. (2017) which evaluate all the possible anthropogenic pollution sources using nitrate isotopes and based on a complete nitrate vulnerability assessment. Groundwater samples



Fig. 14 Distribution of the Grombalia groundwater samples according to their scores for salinization (F1), evaporation (F2) and nitrate pollution (F3). a F2 versus F1. b F3 versus F1. c F3 versus F2

Deringer

with high scores in F1 and low scores in F3 are characterized by high salinity rather than nitrate pollution (quadrant I, Fig. 14b), whereas for quadrant IV (sample nos. 9, 11, 12, 22 and 25), neither salinization effect nor nitrate pollution are responsible of groundwater chemical composition. According to Fig. 14a, c, these last samples, situated in the centre of Grombalia Basin, are affected by evaporation process characterizing by the most enriched isotopic signature ( $\delta^{18}$ O and  $\delta^{2}$ H). Groundwater samples (nos. 4, 5 and 14), located on the positive sides of F1, F2 and F3 axes, are characterized by the higher nitrate values, an enrichment on isotopic composition ( $\delta^{18}$ O and  $\delta^{2}$ H) and high salinity. This highlights that groundwater chemistry for these samples are dominated by irrigation return flow which is affected by three processes: water-rock interactions, evaporation and nitrate pollution.

# Conclusions

Hydrogeochemical, isotopic and geostatistical investigations of Grombalia shallow aquifer permitted to better define the main processes contributing to aquifer mineralization and to assess the impact of human activities on groundwater quality. The hydrochemical data show that the shallow aquifer is essentially characterized by Ca-Mg-Cl/NO3 water type. Aquifer salinization is mostly due to natural processes like water-rock reactions, ion exchange and the dissolution of evaporate minerals such as halite, gypsum and anhydrite. However, high nitrate contents (exceeding 50 mg/l), characterizing the majority of the samples, are mainly caused by the anthropogenic activities as agriculture (possibly associated to agricultural return flow and the widespread use of nitrogen fertilizers) and domestic uses. The stable isotope composition of water reveals the existence of two different groups: (i) the first one characterized by a strong contribution of modern precipitation to aquifer recharge, confirming the recent recharge by rapid infiltration of rainwater, (ii) whereas the second group corresponds to the samples dominated by an evaporation effect, indicating either the slow infiltration of rainwater or the return flow of evaporated irrigation water. Ordinary kriging was applied to describe spatial and temporal behaviour of nitrate concentration data. Nitrate contamination characterizes most of the samples collected in the eastern part of the basin. Principal component analysis (PCA) is in agreement with the findings of the

geochemical and isotopic assessment, highlighting the geochemical processes contributing to groundwater mineralization (water rock interactions, evaporation effect and nitrate pollution). Results also suggest the need for a more rational and effective management of groundwater resources in the Grombalia region, protecting it from contamination risks (i.e. nitrate pollution, salinization) and quality degradation. In this framework, ongoing investigations involve the application of nuclear techniques to improve the understanding of the studied aquifer system, especially in relation to the interactions between the shallow and the deep aquifers and to evaluate its vulnerability to seasonal variations.

Overall current findings are very useful to promote effectiveness of the integrated approaches to tackle the key issues faced by coastal aquifers in arid and semi-arid regions (e.g. salinization, contamination and overexploitation) and to support the correct water resources protection in the long run by promoting science base management practices.

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