



Hydrogeologic and geochemical survey of aquifers based on chemical and isotopic characterisation of groundwater and rain waters: a case study in the Sisseb el Alem Basin (central-east Tunisia)

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Abstract

Chemical and isotopic composition of groundwaters and rain waters in the Sisseb el Alem basin (Tunisia) was monitored to obtain a hydrologic and geochemical characterization of the aquifers. The studied aquifers are the only water resource for domestic and irrigation use in the basin. Two aquifers have been identified by hydrogeologic data, one, shallower, flowing in Plio-Quaternary sediments, the other, deeper, in Miocenic–Oligocenic sediments. Although this area is intensively farmed with widespread fertiliser use and settlements are unsewered, groundwater in the area is relatively uncontaminated by land-use activities. The chemical and isotopic compositions of the sampled waters, which have a meteoric origin, are largely controlled by both the geological signatures of their drainage area and by evaporative processes and water–rock interaction (reverse cationic exchange) phenomena. Geochemical data suggest, on the basis of the Na/Cl, Cl/SO₄ ratios and concentrations of Li, Sr, and Mn, that a hydraulic connection exists between two distinctive aquifers. One strongly influenced by Lake Saadine water characterised by Na/Cl > 1, high Cl/SO₄ and Li, Sr, and Mn > 0.1 meq/l, the other, deeper, characterised by Na/Cl < 1, low and near constant Cl/SO₄ and Li, Sr, and Mn < 0.1 meq/l. Despite relatively high salinity and SAR values, all sampled waters are suitable for irrigation in well-draining soils. The isotopic composition of the rain waters highlights the importance of evaporation in controlling the composition of the groundwater.

Keywords Hydrogeochemistry · Stable isotopes · Sisseb el Alem Basin (Tunisia) · Water budget · Groundwater · Rain water

Introduction

The Sisseb el Alem basin is one of the most important aquifers in Tunisia. However, the recent large considerable increase in water requirements due to demographic and agriculture development has caused an overexploitation of the groundwater resource. Consequently, the elevation of the water table in the region is declining at a rate of about 1.5 m/a (DGRE 2004) which has led to the drying up of many wells in the region.

The overexploitation has caused the quality of the groundwater to deteriorate, and has been exacerbated by the building of the great Nebhana dam and many other small

hill-dams and by a large increase in the number of wells (more than 800) in northern Tunisia (Hamed and Dhahri 2013).

As groundwater is the only water source for potable and agricultural use for local communities in the region, it is important to understand how the local groundwater flow systems function. Geochemical methods are particularly useful tools for understanding groundwater flow processes and can be used to identify processes that alter the quality of the groundwaters during their flow, such as the physical and chemical characteristics of the recharge waters (i.e., meteoric, from artificial reservoirs, and irrigation), the interactions between groundwater and aquifer minerals and pollution from human activities.

The aim of this study is, therefore, to use geochemical techniques to investigate the hydrogeological, chemical, and isotopic characteristics of the groundwaters in the north-western sector of the Sisseb el Alem basin and to model the circulation and recharge of the groundwater that feed

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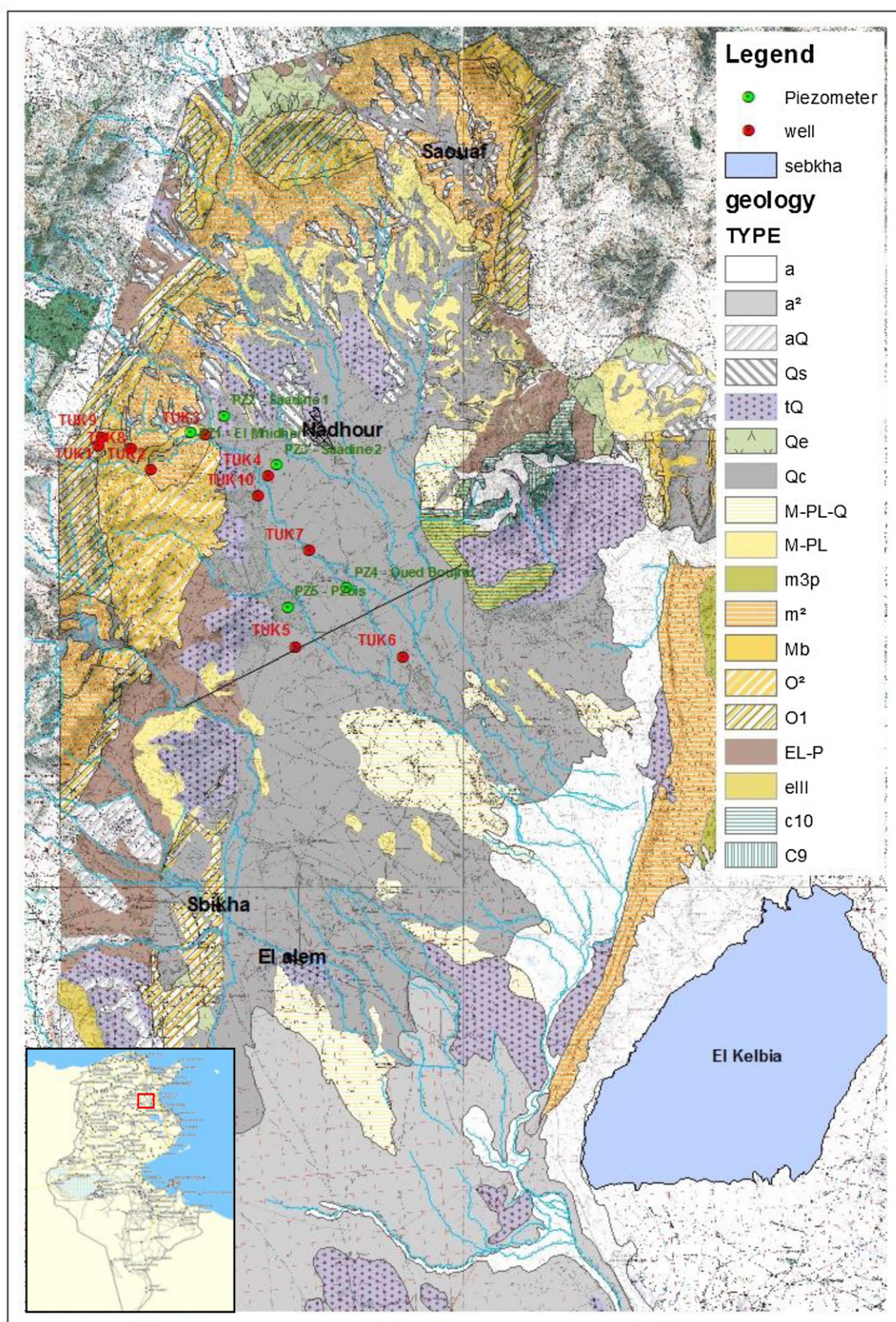


Fig. 1 Geological sketch map of the Sisseb El Alem basin (modified from DGRE 2004). (a) alluvial deposits; (a2) Sebkhia soils; (aQ) alluvial deposits; (Qs) soils; (tQ) terraces and pebbles, Quaternary; (Qe) debris; (Qc) hardpans; (M-PL-Q) continental deposits: clays, sandstones, conglomerates; (M-PL) marine deposits: clays, sandstones, conglomerates; (m3p) alternation of sands or sandstones and marls or clays, Pliocene; (m2) massive sandstones and clays, Tortonian; (Mb) conglomeratic limestones, marly clay sequences, Burdigalian; (O2) sandstones, marls, late Oligocene; (O1) marls, sandstones, early Oligocene; (EL-P) marls, late Eocene; (eIII) limestones, early Eocene; (c10) marls, Maastrichtian; (C9) limestones and marls, Campanian. Points sampled (red circles) are shown. Black line represents the geological cross section line

the plain to the south of Nadhour. For this purpose, four sampling field trips were undertaken to sample the groundwater and surface water bodies in the region. The sampling was carried out from May to December 2010 at time when the piezometric levels of the aquifer were being measured through the piezometric network of the Sisseb area. A rain gauge network was installed to collect isotopic data (δD and $\delta^{18}O$) of precipitations for the period July 2010–November 2011.

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Characteristics of the study area

Geological setting

The Sisseb el Alem basin is located in the eastern part of central Tunisia. It extends from the Kairouan plain to the Zaghouan Mountains. The area studied is delimited to the north by the Nadhour Saouaf syncline, to the south by the plain of Kairouan, to the west by the Bou Morra syncline and the Sbikha monocline, and to the east by the Jebel Fadeloune anticline, the Draa Souatir monocline, and the El Kelbia sabkhet (salt lake) (Fig. 1).

The basin contains sediments of Triassic-to-Quaternary age (Figs. 1, 2). Mesozoic formations crop out in the north of the Nadhour Saouaf syncline on the Zaghouan and Jebel Fadeloune Massifs. Tertiary formations are represented by complete sedimentary series from the Paleocene to the Mio-Pliocene. Limestones, marls, and sandstones dating from the Eocene to the Oligocene outcrop around the alluvial plain of Nadhour-Sisseb. This plain is underlain at shallow depth by fine-to-coarse-grained sediments of Quaternary age. Coarse alluvial deposits in the region are highly permeable.

Quaternary sediments outcrop in the central part of the basin and cover a large portion of the study area. They consist of sands, colluvial sediments, and alluvial sediments in palaeodrainages and in current river systems. Terraces

containing Quaternary sediments also occur in the Nadhour Saouaf synclinal and in the Sisseb Plain.

Sediments in the El Alem basin have been subjected to faulting by different fault systems. These include: a fault system that trends in an NW–SE direction in the Nadhour Saouaf Syncline; the Nebhana inverse fault system that has an NW–SE trend in the western part of the basin, and an N–S-oriented system located in the eastern part of the basin, linked to the subsidence of the El Ketifa anticline, and the downthrown structure of Jebel El Baten. These tectonic activities (opposite structures) that caused the subsidence of the basin began during the Miocene and continued until the Quaternary (Kacem et al. 2008).

Hydrogeological setting

The Sisseb El Alem Basin watershed has an area of about 600 km². It collects waters coming from the northern and western zones of the study area, with the highest contribution coming from Uadi Nebhana which supplies about 35×10^6 m³/year (Kacem et al. 2008).

The Sisseb el Alem aquifer is among the most important water source in Tunisia (Kacem et al. 2008) and is subjected to considerable exploitation which began in 1960 following the construction of the Nebhana Dam and the water pipes utilized for transporting the water from the dam to the Sahel of Sousse. In addition, these pipelines also transfer the water pumped from a series of deep wells. The depletion of the aquifer has worsened since the construction of numerous hill-dam upstream of the basin and with the increase in wells that withdraw water from both the surface and deep aquifers. Furthermore, the overexploitation of groundwater has caused degradation of the quality of water.

Groundwater from the Sisseb El Alem basin lies on a substrate of Upper Eocene gray marls. The depth of the substrate ranges from 200 to 50 m, from upstream to downstream. The basin has subsided by up to of 250 m, and it contains a large volume of stored groundwater in lenticular-shaped permeable formations (Kacem et al. 2008) (Figs. 1, 2).

Three hydrogeological units can be distinguished in the Sisseb el Alem basin:

- The Sisseb hydrogeological unit.
- The El Alem hydrogeological unit.
- The Ketifa El Guelta hydrogeological unit.

The hydrogeological unit of Sisseb is made up of a synclinal structure filled with sediments of Mio-Pliocene-to-Quaternary age which are over 350 m thick. The Sisseb hydrogeological unit is delimited by the buried anticline of Ketifa by a sub-meridian dislocation. Sediments of Eocene-to-Cretaceous rocks have been deposited on the anticline of Kelifa, to form the hydrogeological unit of Ketifa El Guelta.

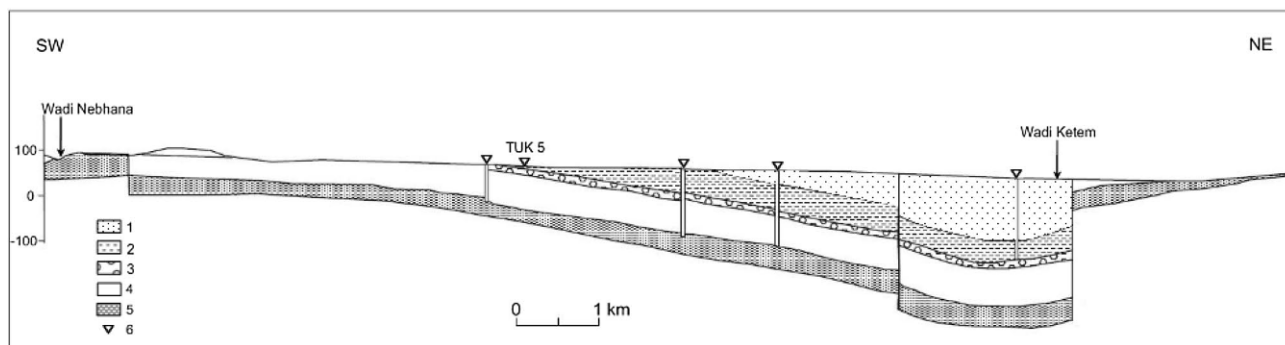


Fig. 2 Geological cross section (modified from Hamza 1992). See Fig. 1 for track. (1) Mio-Plio-Quaternary deposits; (2) marly clay sequences, Burdigalian; (3) conglomeratic limestones, Burdigalian; (4) Oligocene deposits; (5) marls, late Eocene; (6) wells

This unit partially hydraulically connected with the Sisseb basin.

The hydrogeological unit of El Alem is a synclinal structure bordered by two faults: one to the east (the Ketifa fault) and the other on the western side of the structure (Sbikha monoclinical fault).

The hydrogeological unit of El Alem is probably in hydraulic contact with the hydrogeological unit of Sisseb to the north. The El Alem unit is characterised by a relatively coarse matrix in the northern part of the area (Nebhana Wadi El Alem) and which becomes thinner and more clayey in the southern part of the area.

In the study area, two aquifers can be identified: a shallower one and a deeper one. The shallow aquifer consists of variable amounts of sands, gravels, and pebbles. On the western border of the plain, the water table is absent in the unit of Sisseb. The thickness of the superficial aquifer is 15–20 m to the west and decreases to less than 5 m to the east. At El Alem, the aquifer is hosted in the gravel deposits with a thickness of 10–20 m. The aquifer thins and becomes clayey towards south-east (Sogeth 1964). The shallow aquifer is unconfined in the northern and north-western parts of the study area (Sogreah 1960), and is confined in the center part of the basin (Table 1).

To the north of the basin, groundwater hosted in shallow sandy and alluvial sediments shows a static level of the water that is indistinguishable from that of the deep aquifer. The shallow groundwater aquifer is mainly recharged by the infiltration of run-off water through the beds of wadis (Nebhana, El Alem, El Ketifa and Khrioua) along the northern and western boundaries of the plain during rainfall events. The coarse-textured piedmont deposits of the Nadhour region in the northern part of the basin also contribute to the recharge of the shallow aquifer.

The amount of recharge received by the shallow aquifer has been greatly reduced by the construction of the Nebhana dam, which has greatly reduced river flows downstream of the dam. Consequently, the Sisseb El Alem aquifer now

receives only small amounts of recharge, downstream of the dam, which is augmented by spills and leaks from the dam itself. During the period 1967–1995, the Sisseb el Alem plain received less than one-third of the water that historically flowed in rivers in the area before the construction of the dam (Besbes et al. 1996). The deep aquifer belonging to the Sisseb el Alem hydrogeological unit is hosted in the Oligocene and Miocene sandstones. The aquifer consists of two sandstone levels separated by a marly, arenaceous, semipermeable horizon.

The Miocene sandstone levels are massive and coarse, and sometimes brittle. They are interbedded with gray–green marls attributed to the Tortonian. This deep multi-layered aquifer system is a confined groundwater system in hydraulic connection. The Upper Eocene Souar Formation forms a low-permeability base to the deep aquifer. Recharge to the deep aquifer is provided by infiltration through outcrops of Oligocene and Miocene that surround the entire structure upstream of the basin. Recharge to the deep aquifer also takes place by infiltration through the river beds and from leakage from neighboring aquifers (Ain bou Mourra, Chougafia). The top of deep aquifer is more than 70 m deep (Fig. 2).

The availability of water resources in the Sisseb El Alem Basin water resources has been determined through a water balance assessment and in particular the potential surplus water (S) or resource that is available for extractive uses. Table 2 and Fig. 3 show the parameters that describe the water balance that was determined for the basin using the methodology of Thornthwaite and Mather (1957) of Sisseb El Alem Basin. Recharge estimates were determined using rainfall data from the Sbikha meteorological station data for the period 1996–2009 which were taken into account and temperature data from the Kairouan station.

The data obtained are in accord with semi-arid climate conditions and low precipitation of the area. The average annual rainfall for the period 1996–2009 was determined to be 322 mm (Table 2). Precipitation occurs mainly from

Table 1 Hydrological sketch of Kairouan area

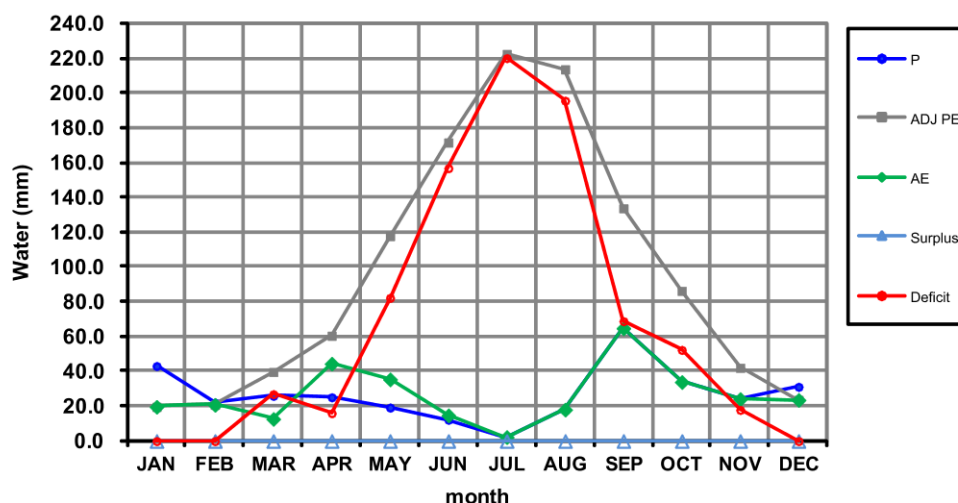
	Formation	Lithology	Age	Reservoir
		Terraces and pebbles, hardpan Alluvial deposits: gravels and sands Ancient alluvial deposits: gravels, clays and sands Debris Reddish sandy clays and sandstones with interbedded conglomerates uncemented (Siciliano)	Quaternary	Aquifer
	Segui	Clays, sandstones and conglomerates	Pliocene	
			Discordance	
	Saouaf	Alternation of sands or sandstones and marls or clays	Miocene	Aquifer
	Beglia	Massive sandstones and clays (Tortoniano)		
	Mahmoudi	Greenish marls and gray-green clays with interbedded glauconitic sandstones		Aquitard
	Ain Ghrab	Conglomeratic limestones, marly clay sequences	Oligocene	Aquifer
		Course sandstones, marls		
		Clays and sandstones		
		Brown sandy clays with ferruginous concretions and thin interbedded sands		
		Cross-stratified sandstones, layers of lignite and glauconitic sandstones		
	Souar	Grey clay marls	Late Eocene	Aquiclude

Table 2 Water budget estimate

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
$T(^{\circ}\text{C})$	12.2	12.7	15.6	18.3	23.3	27.5	30.3	30.5	26.1	22.1	17.0	13.4	20.7
$P(\text{mm})$	43.2	22.0	26.0	25.2	19.3	12.2	2.2	18.1	64.8	33.9	24.1	31.2	322.3
i	3.88	4.12	5.59	7.11	10.29	13.17	15.31	15.42	12.18	9.5	6.37	4.43	107.4
$PE(\text{mm})$	21.8	23.9	38.5	56.0	99.8	146.7	185.4	187.5	129.9	88.1	47.3	26.8	1051.7
$ADJ\ PE(\text{mm})$	19.7	20.8	39.6	60.5	117.8	171.6	222.5	213.7	133.8	86.3	42.1	23.6	1152.0
$P-ADJ\ PE(\text{mm})$	23.5	1.2	-13.6	-35.3	-98.5	-159.4	-220.3	-195.7	-68.9	-52.4	-17.9	7.6	-829.8
$AWL(\text{mm})$	0.0	0.0	-13.6	-49.0	-147.5	-306.9	-527.2	-722.8	-791.8	-844.1	-862.1	0.0	
$SM(\text{mm})$	23.5	24.7	31.8	18.8	2.6	0.1	0.0	0.0	0.0	0.0	0.0	7.6	
$\Delta SM(\text{mm})$	23.5	1.2	13.4	-19.3	-16.2	-2.5	-0.1	0.0	0.0	0.0	0.0	7.6	7.6
$AE(\text{mm})$	19.7	20.8	12.7	44.5	35.4	14.8	2.3	18.1	64.8	33.9	24.1	23.6	314.7
$D(\text{mm})$	0.0	0.0	27.0	16.0	82.4	156.9	220.2	195.7	68.9	52.4	17.9	0.0	837.4
$S(\text{mm})$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

SWC soil water capacity, T monthly mean temperature, P monthly mean precipitation, i monthly heat index, EP monthly potential evapotranspiration, $ADJ\ PE$ adjusted monthly potential evapotranspiration, AWL accumulated potential water loss, SM soil moisture, ΔSM change in soil moisture, AE monthly actual evapotranspiration, D deficit ($ADJ\ PE - AE$), S surplus ($(P - ADJ\ PE) - \Delta SM$)

Fig. 3 Graphical representation of water budget estimate (see Table 2 for details)



September to March–April. The mean annual temperature is about 21 °C with a minimum of 12.2 °C in January and a maximum of 30.5 °C in August. Based on the water balance estimation, the potential evapotranspiration was determined to be about 1200 mm/a (Thornthwaite and Mather 1957). As highlighted in Table 2 and Fig. 3, the region has an annual water deficit of 837 mm.

Sampling and analytical methods

Four groundwater sampling field trips were carried out from May to December 2010. For each field, trip 8 productive deep water-supply wells (TUK2–10) were sampled, as was one dammed reservoir (Lake Saadine: TUK1 and 9) that was used both to artificially recharge the aquifers and to irrigate neighboring areas. All the wells sampled are downhill from the lake and from 1 to 17 km from it. During the last field sampling, three more water samples were collected upstream from the lake: one from a well (TUK11), one from a spring (TUK12), and one from a river (TUK13) (not shown in the figure). The location of the sampled points is given in Fig. 1.

TUK6 well was drained after the field trip in June. Water temperature, pH, electric conductivity (EC), and Eh were measured in the field using ORION 105 (EC) and 250 (pH, Eh) portable instruments and specific electrodes regularly calibrated using specific standard buffers. Water samples for anion determinations (untreated water), and for cation determinations (filtered and acidified with ultrapure HNO_3) were collected and stored in 50–100 cc low-density polyethylene bottles. Analyses were performed using a Dionex ICS1100 ion chromatograph and specific columns for anions (mod. AS14A) and cations (mod. CS12A). Alkalinity was determined by volumetric titration with 0.1 N HCl and methyl orange as indicator. All the analyses exhibited an error below $\pm 3\%$.

Water samples, filtered and acidified with ultrapure HNO_3 , were collected for trace element determinations and stored in 50 cc high-density polyethylene bottles. The analyses were performed using an Agilent 7500 series ICP-MS.

A rain gauge network consisting of 2 stations was installed in the Sisseb El Alem area in June 2010. The stations were installed at different altitudes near Lake Saadin (213 m asl) and at Hir Bgar well 73 m asl near the TUK6 sampling point, in the southern part of the Nadour Plain (Fig. 1). Rain water samples were collected on three occasions in October and November 2010 and in November 2011 (Table 3), and their chemical (i.e., major and minor ions) and isotopic compositions (i.e., $\delta^{18}\text{O}$ and δD) were analyzed. For each sample, the total precipitation volume and mm of rain were estimated.

δD and $\delta^{18}\text{O}$ isotope analyses were performed on the untreated water samples stored in 50 cc low-density polyethylene bottles. These samples were analyzed using an Analytical Precision 2003 Spectrometer for $\delta^{18}\text{O}$ and a Finnigan Delta Plus XP Spectrometer for δD . The oxygen and hydrogen isotope compositions are reported as delta ‰ vs. SMOW values. All the analyses were performed at the Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo laboratories.

The analytical results are given in Tables 3 and 4.

Results and discussion

Chemical composition of groundwater

The groundwater sampled from Sisseb el Alem are characterised by EC values ranging from 1.0 to 3.1 mS/cm, pH values ranging from 7.1 to 7.6, and TDS values ranging from 0.5 to 2.1 g/l. In contrast, the Lake Saadin waters have EC and TDS values which are higher than those of the

Table 3 Chemical and isotopic compositions of sampled groundwaters

Site ID	Easting	Northing	Altitude	Date	T ^o C	pH	EC	Eh	TDS	Ca	Mg	Na	K	HCO ₃	Cl	SO ₄	F	Br	NO ₃	Li	Sr	Mn	δD	δ ¹⁸ O
TUK1	587,841	3,997,377	196	17/05/10	20.0	8.36	4.36	207	3436	20.51	11.55	21.45	0.260	2.40	15.59	34.95	0.090	0.013	0	0.104	0.185	1.15E-03	16	3.80
TUK1				29/06/10	25.5	8.14	4.80	152	3816	21.65	12.85	23.18	0.330	1.80	17.97	40.17	0.100	0.020	0	0.708	0.222	1.26E-02	20	5.19
TUK1				14/10/10	22.0	8.20	5.17	159	4421	26.04	15.09	27.26	0.460	2.00	20.53	46.14	0.110	0.030	0	0.774	0.233	1.74E-02	10	3.34
TUK1				30/11/10	14.3	8.70	2.35	159	1869	14.80	5.08	8.88	0.227	1.40	6.13	20.68	0.060	0.000	0	0.027	0.101	9.46E-04	-17	-3.10
TUK2	590,146	3,916,102	169	17/05/10	22.7	7.17	1.03	165	761	4.94	3.53	2.53	0.080	5.30	3.35	2.35	0.016	0.002	0.03	0.014	0.014	2.55E-05	-28	-5.30
TUK2				29/06/10	23.6	7.23	1.03	85	787	4.90	3.53	3.02	0.090	5.50	3.38	2.40	0.016	0.003	0.03	0.088	0.014	3.04E-05	-29	-5.43
TUK2				14/10/10	22.7	7.30	1.02	76	783	5.06	3.61	2.60	0.097	5.50	3.38	2.41	0.017	0.006	0.03	0.095	0.014	2.39E-05	-31	-5.59
TUK2				30/11/10	23.2	7.23	1.02	106	786	5.05	3.60	2.59	0.090	5.60	3.33	2.39	0.014	0.005	0.04	0.003	0.013	2.47E-05	-33	-5.50
TUK3	592,554	3,997,619	143	17/05/10	20.8	7.55	1.62	236	1112	6.84	3.95	5.96	0.087	4.05	6.91	5.14	0.030	0.004	0.75	0.038	0.062	5.19E-06	-30	-5.30
TUK3				29/06/10	21.8	7.45	1.61	142	1111	6.91	4.01	5.88	0.087	4.10	6.96	5.01	0.030	0.006	0.75	0.215	0.062	1.47E-05	-30	-5.35
TUK3				14/10/10	21.8	7.46	1.62	100	1127	7.01	4.03	5.90	0.090	4.10	7.04	5.20	0.031	0.009	0.77	0.234	0.060	1.85E-05	-30	-5.34
TUK3				30/11/10	21.5	7.37	1.56	82	1137	7.02	4.08	6.01	0.110	4.30	6.92	5.16	0.026	0.010	0.77	0.014	0.060	2.60E-05	-31	-5.00
TUK4	595,332	3,995,784	120	17/05/10	24.9	7.57	1.63	-66	1182	5.26	6.33	6.13	0.122	4.90	5.71	7.32	0.027	0.006	0	0.030	0.033	1.14E-03	-28	-5.40
TUK4				14/10/10	24.8	7.45	1.59	-13	1212	5.46	6.56	6.22	0.130	4.90	5.86	7.64	0.021	0.010	0	0.204	0.036	1.36E-03	-33	-5.35
TUK4				30/11/10	21.9	7.50	1.58	-63	1220	5.47	6.60	6.28	0.130	5.00	5.81	7.67	0.026	0.007	0	0.002	0.036	1.29E-03	-32	-5.00
TUK5	596,553	3,987,691	85	18/05/10	22.8	7.22	3.05	138	2106	7.91	8.23	16.29	0.160	4.40	15.80	11.87	0.050	0.011	1.06	0.060	0.069	1.46E-05	-29	-5.40
TUK5				28/06/10	22.9	7.27	3.07	161	2125	8.05	8.26	16.13	0.170	4.80	15.76	11.82	0.050	0.020	1.03	0.352	0.070	2.23E-05	-30	-5.30
TUK5				13/10/10	22.7	7.11	3.11	162	2160	8.36	8.51	16.56	0.230	4.80	15.94	11.91	0.040	0.020	1.08	0.398	0.068	2.62E-05	-31	-5.42
TUK5				30/11/10	22.2	7.17	3.00	56	2088	8.16	8.35	16.41	0.150	4.60	15.08	11.64	0.040	0.010	1.03	0.007	0.068	2.06E-04	-33	-5.00
TUK6	601,329	3,987,760	72	18/05/10	24.0	7.44	1.53	50	1089	3.49	3.11	9.33	0.110	5.10	6.39	4.21	0.056	0.003	0.35	0.040	0.031	4.45E-05	-33	-5.80
TUK6				29/06/10	24.0	7.44	1.55	67	1113	3.97	3.36	8.97	0.110	5.20	6.25	4.62	0.053	0.009	0.32	0.219	0.033	3.10E-05	-33	-5.62
TUK7	597,216	3,992,473	101	18/05/10	22.2	7.43	1.75		1369	6.00	4.88	9.72	0.110	5.10	8.42	7.07	0.037	0.011	0.17	0.039	0.041	9.90E-06	-31	-6.00
TUK7				29/06/10	22.3	7.39	1.89	138	1366	5.90	4.90	9.81	0.110	4.90	8.54	7.15	0.035	0.012	0.18	0.230	0.041	1.04E-05	-32	-5.59
TUK7				13/10/10	22.0	7.27	1.54	118	1196	6.22	4.88	6.57	0.110	4.70	5.70	7.17	0.033	0.008	0.36	0.222	0.045	1.56E-05	-33	-5.72
TUK7				30/11/10	21.4	7.30	1.55	148	1172	6.53	4.99	6.04	0.110	4.50	5.38	7.22	0.022	0.007	0.39	0.014	0.043	1.94E-05	-33	-5.50
TUK8	589,240	3,997,003	176	18/05/10	20.9	7.23	2.48	38	1827	11.13	6.24	10.54	0.100	3.60	9.35	15.00	0.050	0.002	0.15	0.064	0.123	9.81E-04	-22	-3.50
TUK8				29/06/10	25.9	7.22	2.17	64	1581	8.80	5.81	9.44	0.110	4.00	8.11	12.01	0.040	0.008	0.04	0.350	0.095	1.57E-04	-25	-4.46
TUK8				14/10/10	20.7	7.28	2.56	34	1881	11.61	6.45	10.61	0.122	4.20	9.41	15.05	0.030	0.010	0.11	0.494	0.142	6.55E-04	-22	-3.36
TUK8				30/11/10	20.7	7.18	2.44	38	1893	11.57	6.53	10.80	0.140	3.70	9.59	15.63	0.050	0.000	0.17	0.004	0.129	7.36E-04	-22	-3.10
TUK9	587,924	3,997,061	187	18/05/10	18.9	8.22	4.33	77	3460	20.38	11.72	21.52	0.270	2.40	15.83	35.26	0.089	0.011	0	0.111	0.189	1.29E-03	15	4.00
TUK10	594,887	3,994,448	187	29/06/10	26.9	7.17	2.26	-21	1638	6.33	6.50	11.88	0.140	5.00	8.27	11.39	0.040	0.013	0.10	0.263	0.063	5.23E-04	-29	-5.08
TUK10				12/10/10	24.8	7.19	2.25	4	1641	6.28	6.44	11.84	0.150	5.30	8.09	11.26	0.047	0.012	0.10	0.310	0.065	7.73E-04	-31	-5.26
TUK10				30/11/10	23.7	7.21	2.14	10	1682	6.38	6.62	12.26	0.180	5.50	8.27	11.31	0.030	0.006	0.18	0.002	0.065	6.27E-04	-32	-4.90
TUK11	n.d	n.d	n.d	01/12/10	n.d	n.d	n.d	n.d	1212	6.62	5.44	9.00	1.531	4.80	10.01	4.84	0.013	0.016	2.53	n.d	n.d	n.d	n.d	n.d
TUK12	n.d	n.d	n.d	01/12/10	n.d	n.d	n.d	n.d	259	3.58	1.74	1.60	0.135	4.20	1.53	1.05	n.d	n.d	0.31	0.028	n.d	n.d	n.d	n.d
TUK13	n.d	n.d	n.d	01/12/10	n.d	n.d	n.d	n.d	1296	7.61	3.53	12.36	0.202	3.50	12.73	7.38	0.043	0.008	0.02	0.065	n.d	n.d	n.d	n.d

TDS is in mg/l, elemental concentrations in meq/l, and δD and δ¹⁸O in ‰ vs SMOW

Table 4 Chemical and isotopic compositions of rain waters

Site ID	Easting	Northing	Altitude	Date	TDS	Ca	Mg	Na	K	HCO ₃	Cl	SO ₄	F	NO ₃	δD	δ ¹⁸ O
TPL1	601,278	3,987,724	73	13/10/10	74	30.86	0.94	3.45	3.722	24.41	5.32	4.61	0.055	0.93	-16	-3.87
TPL1				29/11/10	38	7.85	0.44	1.15	0.759	24.41	1.99	1.17	0.015	0.00	-42	-7.43
TPL1				12/10/11	53	39.68	1.23	3.11	2.401	0.00	4.88	1.29	0.029	0.00	-20	-3.84
TPL2	587,920		213	14/10/10	42	19.84	0.70	2.19	1.509	12.20	3.43	2.50	0.038	0.00	-29	-5.48
TPL2				29/11/10	21	3.37	0.36	1.37	0.543	12.20	2.24	1.35	0.011	0.00	-30	-6.03
TPL2				12/10/11	36	20.31	1.41	2.79	0.880	0.00	4.35	6.08	0.029	0.00	-23	-4.19
TPL3	670,554		21	11/10/10	92	20.04	1.54	7.59	5.357	36.61	14.18	6.24	0.038	0.00	-24	-4.59
TPL3				29/11/10	62	11.99	0.67	3.57	1.533	36.61	6.04	1.05	0.015	0.19	-33	-6.28
TPL3				11/10/11	62	37.46	1.73	6.32	4.035	0.00	10.41	1.79	0.046	0.00	-21	-4.30

ECs are in mS/cm, Eh in mV, TDS in mg/l, elemental concentrations in meq/l, and δD and δ¹⁸O in ‰ vs SMOW

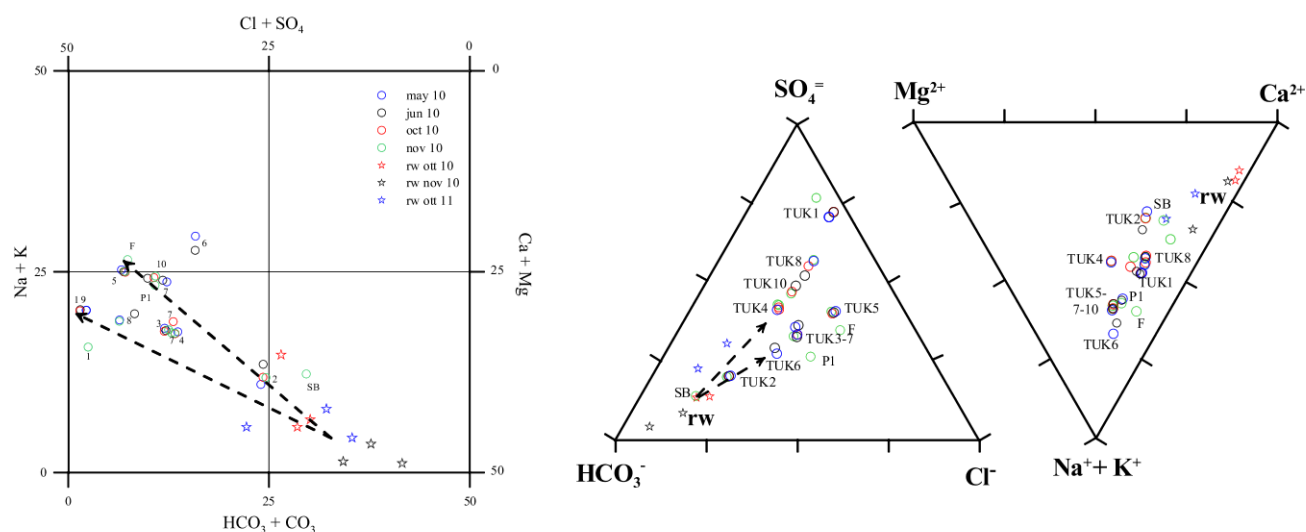
groundwater samples (i.e., 2.3–5.1 mS/cm and 1.9–4.4 g/l, respectively) and alkaline pH values (> 8).

The major ions in the groundwater samples were plotted on the Langelier–Ludwig classificative diagram to distinguish between the different water types in the aquifer as a function of the chemical composition of the groundwater. Almost all the waters collected belong to the Cl-SO₄-earth alkaline facies, excluding some samples which instead belong to the Cl-SO₄-alkalines (TUK6, TUK5, and TUK13) and to the HCO₃-earth alkaline facies (TUK2, TUK12) (Fig. 4). Alkalines are the dominant cations in the TUK13 and TUK6 samples; SO₄ is the dominant anion in the TUK1 and TUK8 samples, while Cl is the dominant anion in the TUK11 and TUK13 samples.

The water samples show an important difference in EC, major and minor, although mainly in the Li, Sr, and Mn elements.

Almost all the waters sampled show a rough uniformity in composition during the sampling period (reflecting the uniformity of the rock compositions) with the exception of the lake waters (TUK1). The TUK1 samples collected in summer (i.e., dry and warm period) have higher TDS values than those sampled during the winter. These differences may have been caused by evaporative phenomena, which are very strong in summer.

On the Na/Cl plot (Fig. 5), which is often utilized to identify processes responsible for water salinity (Magaritz et al. 1981; Dixon and Chiswell 1992; Guendouz et al. 2002; Kamel et al. 2011), the samples follow two main trends. The first of these trends is along the halite dilution line (i.e., where the molar Na/Cl ratio = 1) with rain water and TUK5 as end-members. The second trend is characterised by a molar Na/Cl ratio of > 1 which TUK1 as end-members.

**Fig. 4** Langelier–Ludwig classificative diagram (on the left); anion and cation triangular plot (on the right)

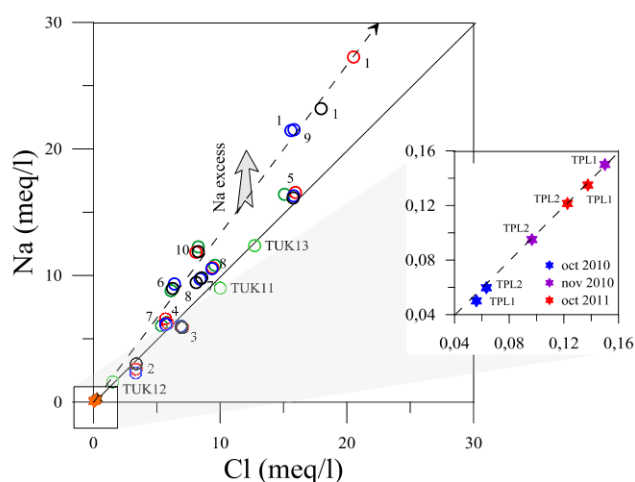
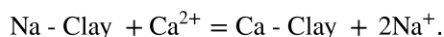


Fig. 5 Sodium and chlorine concentration (in meq/l) in the sampled waters. The straight line represents $\text{Na}/\text{Cl}=1$; the dotted line represents $\text{Na}/\text{Cl}>1$. Zoomed plot is for rain water samples. Symbols as in Fig. 4

The ‘Na excess’ ($\text{Na}/\text{Cl}>1$) in the waters, strongly evident in TUK1 (Fig. 5), could be due to the combined effects of two processes:

1. The increase in Ca and HCO_3^- in the groundwater due to evaporative concentration and testified by the supersaturation of CaCO_3 in the water samples, as highlighted by the saturation index ($\text{SI}>1$) (AQUACHEM ver 4.0, Waterloo Hydrogeologic 2003).
2. Cation-exchange phenomena between groundwater and clay levels (Abid et al. 2011).

Both processes have, as a result, a Ca–Na exchange in the clays and, accordingly, an increase in the Na/Cl (>1) ratio in the groundwater (Vengosh and Rosenthal 1994 and references therein; Montoroi et al. 2002):



Ca adsorption from clays causes an increase in dissolved SO_4 and, consequently, an increase in SO_4/Ca and SO_4/Cl ratios (>1) (Figs. 4, 6). This behaviour is supported by the slope of the trend shown in the plot of $\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- - \text{SO}_4^{2-}$ versus $\text{Na}^+ + \text{K}^+ - \text{Cl}^-$ (in milliequivalents per litre, Fig. 6). Indeed, an increase in the alkalis (i.e., Na and K) corresponds to a decrease in alkaline earth elements (Ca and Mg) (Garcia et al. 2001). The absence of cation exchanges in samples with $\text{Na}/\text{Cl}=1$ testifies to their position near the origin of the Cartesian axes (McLean et al. 2000).

Trace and minor elements in the sampled groundwaters tend to be more characteristic of different lithology and hydrogeological properties of the aquifer than of major elements.

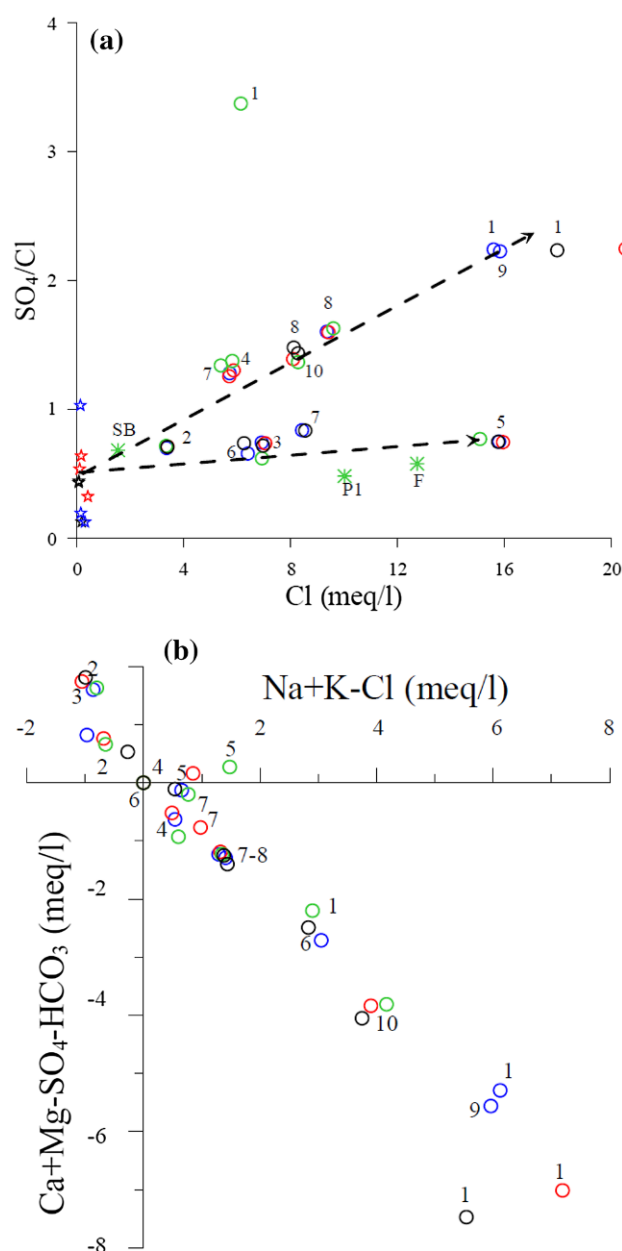


Fig. 6 **a** Water samples shift from meteoric to Lake (TUK1) and to TUK5; sample's alignments are highlighted by arrows. Asterisks represent local meteoric waters and **b** relationship between $(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})$ and $(\text{Na}^+ + \text{K}^+ - \text{Cl}^-)$ reflecting the cation-exchange processes. The debit or surplus of $(\text{Na}^+ + \text{K}^+)$ respect Cl^- ions is balanced by the corresponding changes of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ over the $(\text{HCO}_3^- + \text{SO}_4^{2-})$ ions. Concentrations are in meq/l. Symbols as in Fig. 4

Furthermore, the behaviours of Li, Sr (Fig. 7), and even more so of Mn (Fig. 8) imply the same groundwater assemblage.

In particular, the Mn concentrations which are higher than 0.0001 meq/l characterise the “TUK1 end-member assemblage”, whereas the “TUK5

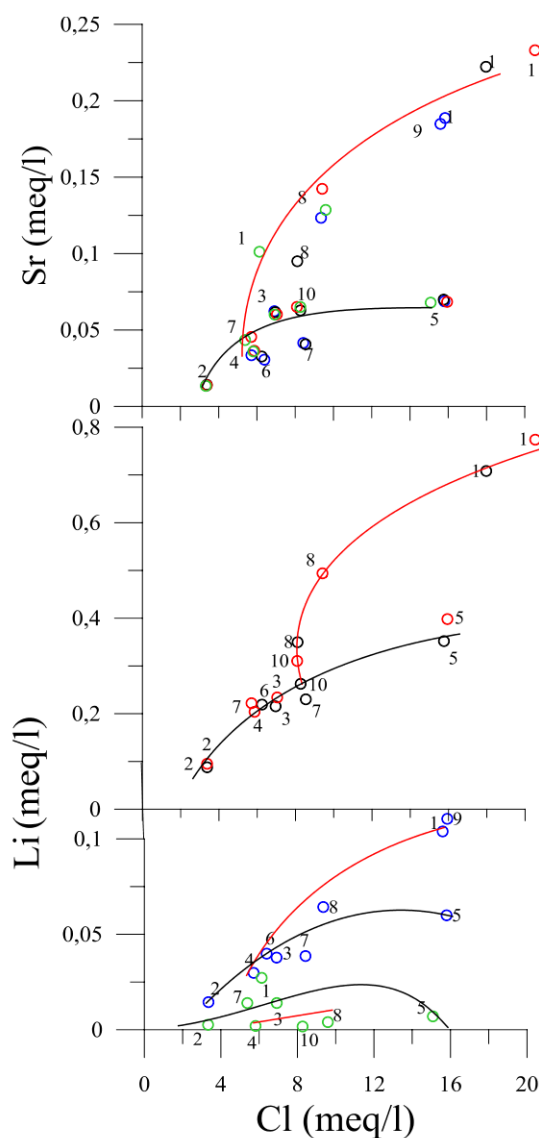


Fig. 7 Lithium and strontium concentrations with respect to chlorine. Concentrations are in meq/l. Symbols as in Fig. 4

end-member assemblage” is characterised by Mn having a value < 0.0001 meq/l.

The calculated values of the sodium adsorption ratio ($SAR = Na / ((Ca + Mg) / 2)^{1/2}$) and measured EC values indicate that the studied waters have a “low-medium sodium ion (S1–C3, S1–C4) and “high electric conductivity (S2–C4) values with the exception of TUK1, TUK9, and TUK5 that are classified as having a “high” sodium content and a “very high” electric conductivity (S3–C4; Fig. 9). This indicates that the water would be suitable for irrigation use in the well-draining (high permeability) soils typical of this area (mainly sands and sandstones).

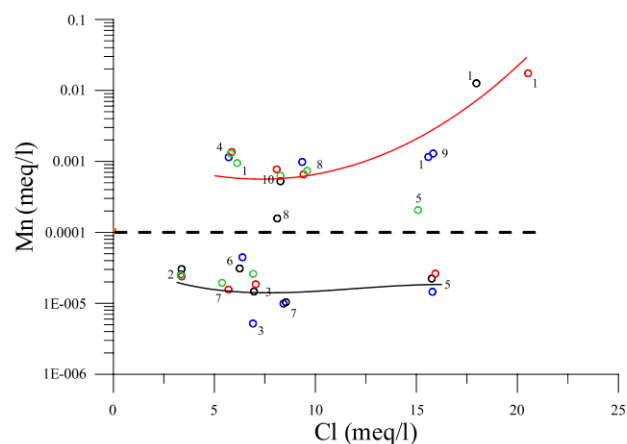


Fig. 8 Manganese concentration with respect to chlorine. The main alignments are highlighted by red and black lines. The dashed line represents the border value to distinguish the two groups of ground-water. Concentrations are in meq/l, symbols as in Fig. 4

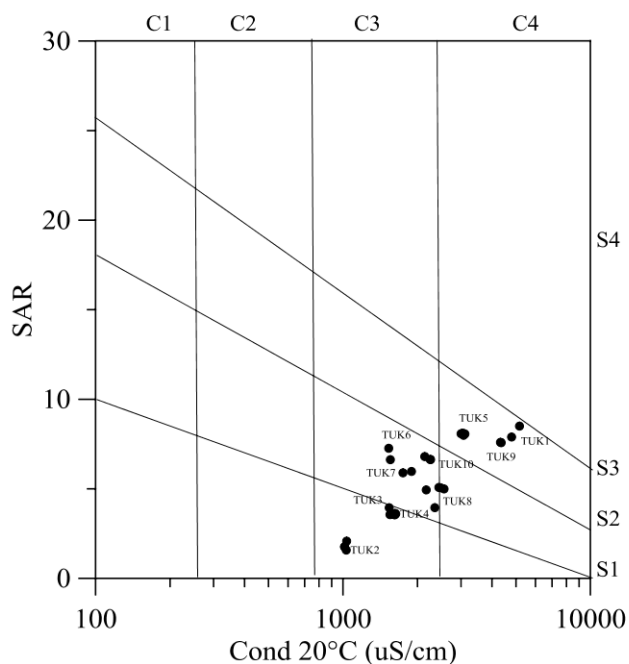


Fig. 9 Wilcox classifier diagram showing the irrigational suitability of sample waters

Chemical composition of rain waters

The chemical composition of the bulk rain waters sampled in the studied area is dominated by Ca, Cl, and HCO_3 as the main elements (Fig. 4). The high Ca and HCO_3 levels are likely to have been derived from the dissolution of carbonate aeolian dust particles.

The chloride (Fig. 5) in rainwater is likely to have originated from sea spray or from the dissolution of halite dust particles. The low concentration of SO_4 and NO_3 testifies

to the near absence of factories and intensive agricultural activities (Fig. 10) in the region. The higher concentration of Ca by comparison with Cl suggests a predominant continental origin of the meteoric waters.

The salt concentrations in the sampled meteoric waters are influenced by the total bulk of rainfall. The rainfall sampled in June–September (46 mm) had much higher concentrations than those relating to the period October–November 2010 (110 mm) differences in the amount of rainfall received during this period (Fig. 11).

The third sampling campaign, which represents the bulk composition of 11 months of rainfall (from November 2010

to September 2011), can be considered to be a “weighted averaged” rain water composition.

Isotopic composition of rain water and groundwater

The climatic (Mediterranean climate along the coast, Saharan desert inland) and geographic (lack of important reliefs) factors influence the air masses that provide rainfall and the chemical composition of rainwater in the region (Celle-Jeanton et al. 2001a, b). In particular, rainfall linked to air masses coming from Mediterranean areas are more abundant in volume and have higher levels of in $\delta^{18}\text{O}$ by comparison with

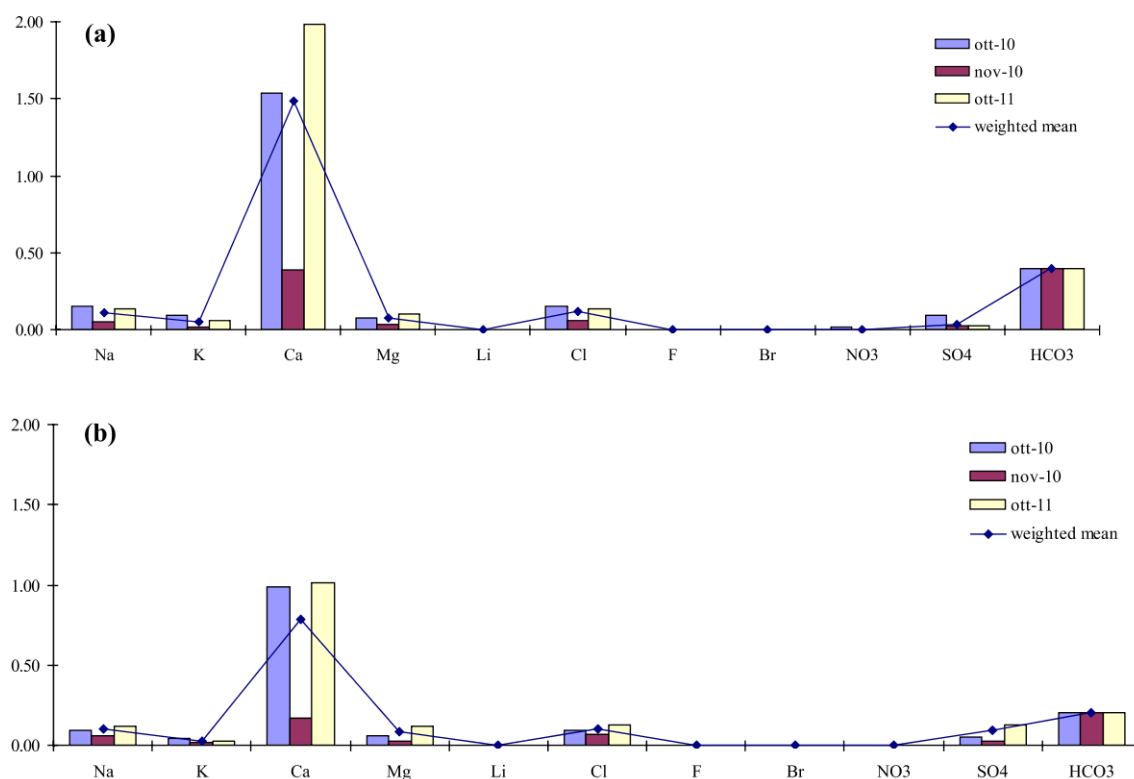


Fig. 10 Concentration of major elements in rain water in **a** TPL1 and **b** TPL2 Stations. Concentrations are in meq/l. Weighted average concentrations are also shown

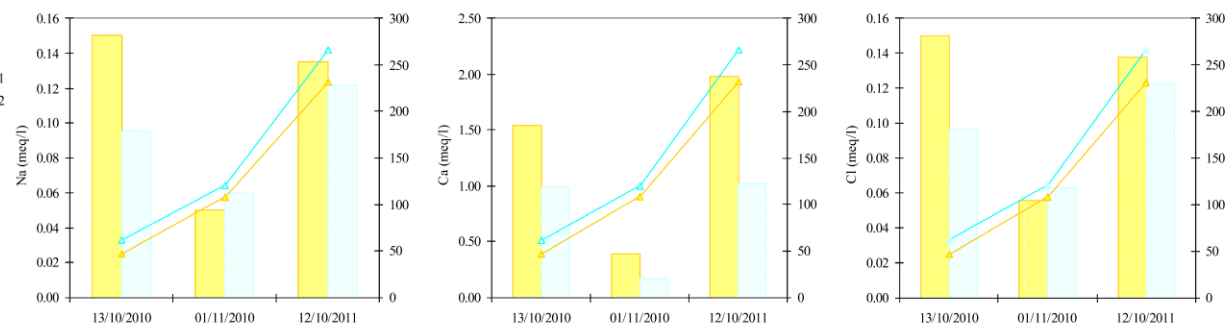


Fig. 11 Na, Ca, and Cl concentration in rain water (histogram) and rain amount (line)

rainfall of Atlantic origin which is a much smaller proportion of the rainfall total and has smaller amounts of ^{18}O due to the continental effect. Climatic influences on the isotopic compositions of rain water are visible on the local meteoric water lines (LMWLs, Fig. 12a) defined for Sfax ($\delta\text{D}=6.4\ \delta^{18}\text{O}+5.2$) and Tunis ($\delta\text{D}=6.7\ \delta^{18}\text{O}+3.5$) (Celle-Jeanton et al. 2001a, b).

The slope of the LMWLs is lower than that of the Global and Mediterranean Meteoric Water Line, which is the result of kinetic isotopic fractionation of the rainwater induced by evaporation processes during the fall of the rainwater itself (Celle-Jeanton et al. 2001a, b; Ben Hamouda et al. 2011; Fehdi et al. 2011).

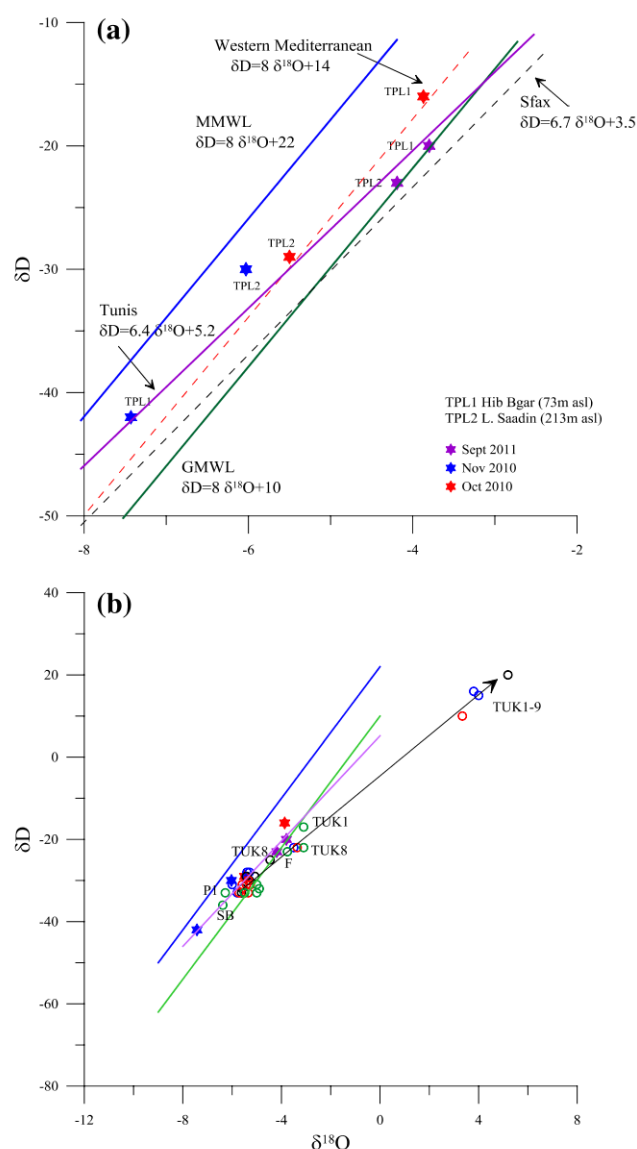


Fig. 12 δD and $\delta^{18}\text{O}$ relationship in rain waters (a) and in groundwater (b)

The isotopic values of the rain water collected in our rain gauge network plot between the MMWL (Gat and Carmi 1970; Gat 1980) and the GMWL and remain close to the local meteoric water line (LMWL) of Sfax and Tunis (Fig. 12).

Of all the samples of rain water collected, the most negative samples from November 2010 are probably less fractionated than the others and can be considered representative of local precipitations in both the Lake Saadine area (TPL2) and on the plain (TPL1).

Samples from September 2010 (representative of rain water falling from June 28th to October 13th 2010) and September 2011 (representative of rain water falling from November 30th 2010 to October 12th 2011) are more positive and have probably been influenced by the high level of evaporation during the summer months (high T and dry conditions). In particular, the sample collected in September 2011 can be considered the annual average isotopic composition of the rain waters. The isotopic composition of δD and $\delta^{18}\text{O}$ of the rain waters from TPL1 (i.e., from the plain) ranges from -3.8 to -7.4‰ in $\delta^{18}\text{O}$ and from -16 to -42‰ in δD , while that of TPL2 (i.e. at the lake), which is located at a higher altitude, shows smaller variations ($-6 < \delta^{18}\text{O} < -4$ and $-20 < \delta\text{D} < -30\text{‰}$, Table 3).

The D-excess values reflect the evaporative effect described above and show values which are typical of rain coming from Mediterranean areas (Celle-Jeanton et al. 2001a, b).

The isotopic composition of the groundwaters in the Sisseb El Alem area ranges from -3.8 to -7.4‰ in $\delta^{18}\text{O}$ and from -16 to -42‰ in δD (Table 3). Almost all the groundwater plots inside the MMWL and the GMWL show values which are slightly more positive in δD and $\delta^{18}\text{O}$ than those of rain water. This phenomenon, which is more evident in the November samples, indicates a subsequent/further evaporation process during the infiltration of rain water into the soil. In detail, it is possible to note a gradual increase in $\delta^{18}\text{O}$ in the samples collected between May 2010 and November 2011. This behaviour is evident especially in the TUK8 samples and in the lake (TUK1-9) samples (Fig. 12b) that arrange (themselves) on an evaporation curve/line with the equation $\delta\text{D}=4.85\ \delta^{18}\text{O}-4.7$ (best fit line).

Conclusions

The Sisseb El Alem is one of the most important water basins in northeast Tunisia. The basin contains sediments of Triassic-to-Quaternary age. The assessment of the water resources carried out for the basin has permitted us to estimate that the system does not have any water surplus. The over exploitation which began in the 60s, together with the absence of any water surplus, have resulted in the

deterioration of the chemical quality of the groundwaters and reduction of potentiometric heads in the aquifers by up to 1.5 m/a.

The chemical and isotopic compositions of the waters sampled in the Sisseb El Alem basin (rain waters, shallow, and groundwater) reflect the climatic characteristics of a semi-arid with limited rainfall (about 322 mm/a) and high annual mean temperature (21 °C). The most evident effect is evaporation involving rain water during the different phases of groundwater recharge, both during the descent of the rain itself towards the ground and during its infiltration into the soil.

The chemical composition of groundwater in the area is dominated by alkaline earth elements and chloride and are characterised by high EC values. Despite the high EC level, on the basis of SAR values, groundwater in the area is suitable for irrigation use.

Based on the geological setting and the hydrochemical characteristics of groundwater, the hydrogeology of the studied area can be described as follows:

- a shallower, mostly unconfined aquifer that is influenced directly by (i) the effects of evaporation and (ii) the infiltration of hypersaline waters from Lake Saadine and represented by the TUK1, TUK4, TUK8, TUK9, and TUK10 samples. It is strongly influenced by cationic exchange phenomena with the Burdigalian clays forming the substrate. The samples are characterised by high Na/Cl and SO_4/Cl ratios, high Li and Mn, and low Sr contents;
- a deeper aquifer represented by the TUK2, TUK3, TUK5, TUK6, and TUK7 samples, characterised by low Na/Cl and SO_4/Cl ratios, low Li and Mn, and high Sr content.

The TUK4 and TUK7 samples show an anomalous behaviour with respect to the other samples. In fact, they are not always attributable to a specific, shallow or deep, aquifer. This anomaly is probably due to the fact that in the plain, in correspondence of these wells, in some period of the year, the two aquifers are connected to each other showing intermediate composition between the shallower and the deeper aquifers.

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