Research Article

Characterization of Recharge Mechanisms and Sources of Groundwater Salinization in Ras Jbel Coastal Aquifer (Northeast Tunisia) Using Hydrogeochemical Tools, Environmental Isotopes, GIS, and Statistics

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Groundwater is among the most available water resources in Tunisia; it is a vital natural resource in arid and semiarid regions. Located in north-eastern Tunisia, the Metline-Ras Jbel-Raf Raf aquifer is a mio-plio-quaternary shallow coastal aquifer, where groundwater is the most important source of water supply. The major ion hydrochemistry and environmental isotope composition ($\delta^{18}\text{O}$, $\delta^2\text{H}$) were investigated to identify the recharge sources and processes that affect the groundwater salinization. The combination of hydrogeochemical, isotopic, statistical, and GIS approaches demonstrates that the salinity and the groundwater composition are largely controlled by the water-rock interaction particularly the dissolution of evaporate minerals and the ion exchange process, the return flow of the irrigation water, agricultural fertilizers, and finally saltwater intrusion which started before 1980 and which is partially mitigated by the artificial recharge since 1993. As for the stable isotope signatures, results showed that groundwater samples lay on and around the local meteoric water line LMWL; hence, this arrangement signifies that the recharge of the Ras Jbel aquifer is ensured by recent recharge from Mediterranean air masses.

1. Introduction

The hydrogeology of coastal aquifers has been studied intensively during the past decades, stimulated by both scientific interest and societal relevance [1]. Coastal areas throughout the Mediterranean face salinization problems of groundwater which is the major source of water supply especially for drinking and agricultural sector. The imbalance between abstraction and natural recharge rates causes an overexploitation of groundwater resources resulting in declining groundwater table, water quality degradation, and crop damage.

A number of aquifers in coastal zones are being increasingly exploited and affected ([2–6]). For instance, groundwater contamination and decline of water levels have been reported in Tunisia [7–13] and in many countries around the

world. It has been reported in India [14], Jordan [15], Australia [16], USA [17], China ([18, 19]), Netherland [1], and among many others.

In semiarid coastal regions of north-eastern Tunisia, such as Ras Jbel plain, the groundwater is usually the main resource used for irrigation and drinking purposes. Nevertheless, salinization is becoming a common problem affecting groundwater resources. Groundwater exploitation of the Ras Jbel aquifer began in 1949 and has increased each year since 1980. Under pressures of population, climate change, and pollution, the aquifer faces substantial challenges in the management of scarce freshwater resources. During the last four decades, the shallow aquifer groundwater has been over-exploited through excessive, uncontrolled pumping mainly for domestic and agricultural purposes [20]. Salinization

FIGURE 1: Geological and location map of the study area [28–30].

due to seawater intrusion and decreasing groundwater levels has recently been identified [21]. Unplanned and substantial withdrawals of groundwater from the shallow aquifer of Ras Jbel have resulted in severe water level decline of up to 7 m in some areas and high total dissolved solids (TDS) contents reaching 8000 mg/l. Reports of increasing salinity of groundwater supplies in the area suggest a need to define the sources of salt water. It is also useful to study the recharge mechanisms as well as the mixing fresh water/saline water.

Stable isotope and geochemical techniques have been used in groundwater studies of coastal aquifers worldwide [22–25] for determining the origins of groundwater salinization in aquifers and processes that affect water chemistry, such as rock weathering, evaporation, atmospheric precipitation, and cation exchange. Consequently, studying stable isotope and geochemical techniques can significantly improve our understanding of groundwater hydrodynamical processes and chemical evolution [26]. In the present study, environmental isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$) in conjunction with hydrochemistry (major ions) were employed (1) to define the potential sources and different mechanisms of groundwater salinization in the study area (2) to discuss the chemical evolution of groundwater and (3) to explain groundwater recharge and discharge in the coastal plain of Metline- Ras Jbel- Raf Raf.

2. Study Area

The Metline-Ras Jbel-Raf Raf plain, which covers a total area of about 50 km², represents one of the most important

FIGURE 2: Yearly precipitation in Metline-Ras Jbel-Raf Raf plain [64, 65].

agricultural regions in north-eastern Tunisia (Figure 1). It is characterized by a semiarid, “Mediterranean” climate with mild, wet winters and warm, dry summers [27, 28]. The average annual precipitation ranges from approximately 258 to 993 mm (Figure 2). Geologically, it is limited to the south by Jbel Djaouf, En Nadhour, and Ed Demina, to the southwest by Jbel Sidi Saleh, Hakima, and El Faouar, to northwest by Jbel Bab Banzart, Sidi Bou Choucha, and Touchela, to the north and northeast by the Mediterranean sea. The plain of Metline-Ras Jbel-Raf Raf is a wide basin of collapse, formed by a subsidence followed by an alluvial and recent sedimentation. It is affected by folding and faults in NW-SE and SSW-NNE directions. Sedimentary series extend from Miocene to Quaternary. The lithological description of these sediments [28–30] reveals that the Miocene is represented by the Kechabta

FIGURE 3: Evolution of the exploitation rate and the monitoring well number of the shallow aquifer of Ras Jbel during 1966 and 2005 [30, 31].

and Wadi Bel Khedim formations. The Kechabta formation has a thickness of about 1000 m and consists of alternation of marls and fine sandstone benches. The Wadi Bel Khedim formation is of 250 m thickness. At the east of Raf Raf, it is composed of large outcrops of gray marls with gypsum benches. The Quaternary series unconformably overlies the Miocene series and is divided into seven units (from bottom to the top qm^1 , Aa, qm^2 , Qp^a , $Qp-t$, D and a).

Hydrologically, the Quaternary series and the current formations, characterized by their extension and their good permeability, host the shallow aquifer of Ras Jbel. This aquifer is recharged by local infiltration on the plain, by water flowing from the surrounding hills, and from the different rivers crossing the plain: Wadi Beni Ata and Wadi Ali in Beni Ata region, Wadi El Kantra, El Blaati, and El Ma in Ras Jbel region, Wadi Sandid draining the zone of Raf Raf and Wadi El Kantra in the region of Dar El Khaddar. Pumping tests showed that transmissivity can reach $15 \cdot 10^{-4} \text{ m}^2/\text{s}$. The most transmissive areas are the low alluvial plain of Bahirat Beni Ata, the low alluvial area of Wadi El Krib and El Aouinet, and the upstream area of Ain Cherchar, Ain Ezzaouia, Ain Kassa, and Ain El Hammam, as well as the sandstone dune of Ain El Mestir and Ain Mahloul.

The shallow aquifer of Ras Jbel is affected by natural and anthropogenic factors like evaporation, irrigation, pumping, and so forth. The aquifer is tapped by several private and state owned wells. In the period between 1985 and 1990, the exploitation rate was estimated at $13.5 \text{ Mm}^3/\text{year}$, which exceeded the renewable resources evaluated at $8.44 \text{ Mm}^3/\text{year}$ [31]. The total number of dug wells has been estimated to be 1387 in 1985, 1396 in 1990, and 1563 in 2005. In 2005, the exploitation rate was estimated at $10.27 \text{ Mm}^3/\text{year}$ (Figure 3). The massive exploitation of aquifer resources in response to the heavy pumping caused a drop in the water level (Figure 4) and the deterioration of water quality. In 1949, the salinity of the groundwater varied between 648 and 1692 mg/l [32]. The investigations carried out by the DGRE between 1985 and 1993 through several monitoring wells revealed the existence of a very saline groundwater. The degradation of the water quality has been detected mainly in coastal areas where salt concentrations exceeded 15 g/l in 1985

and 8 g/l in 1993 and in the depression of Bahirat Beni Ata where the ante-quaternary substratum is below the sea level [21].

3. Methods

3.1. Water Sampling and Chemical Analysis. Ninety-four samples (including pumping wells and piezometers) were collected for geochemical analysis (major elements) and isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$) during the wet and the dry season of March and July 2007 (Figure 5). Sampling locations were recorded using a portable GPS device. Prior to sampling, all wells were pumped for several minutes to eliminate the influence from stagnant water. Samples were collected in cleaned polyethylene bottles, tightly capped and stored at 4°C until analysis. Electrical conductivity (EC), salinity, and pH were measured in the field using a portable conductivity, salinity, and pH meter.

Chemical analyses were done using a Varian 730-ES ICP Optical Emission Spectrometer for cations and using ion chromatography (DX-120, Dionex, USA) for anions. HCO_3^- was measured by titration (Hach, USA). Samples for stable isotope analysis were collected according to the procedures described by Clark and Fritz [33]. Isotopic analyses were conducted in the isotopic laboratory of the department of Hydrology and Geo-environmental Sciences of the Faculty of Earth and Life Sciences of the Free University of Amsterdam. Isotopic ratios are expressed in per mil (δ) and oxygen and hydrogen isotope analyses were reported to d notation relative to Vienna Standard Mean Oceanic Water (V-SMOW), where $d = [(R_s/R_{\text{VSMOW}}) - 1] \times 1000$, R_s represents either the $^{18}\text{O}/^{16}\text{O}$ or the $^2\text{H}/^1\text{H}$ ratio of the sample, and R_{VSMOW} is $^{18}\text{O}/^{16}\text{O}$ or the $^2\text{H}/^1\text{H}$ ratio of the SMOW. Typical precisions are ± 0.1 and $\pm 1\%$ for oxygen-18 and deuterium, respectively.

3.2. Statistical Analysis. The physicochemical parameters and chemical composition of the groundwater samples are presented in Table 1. All the acquired data were integrated into hydrogeochemical database in order to study the groundwater quality and to identify the groundwater salinization processes that contributed to the acquisition of the actual chemical composition.

Piper plots [34], considered as the common method for a multiple analyses on the same graph, are used to represent the different water samples and to distinguish graphically between different water types defined by the Stuyfzand classification (1993). Sample points with similar hydrochemistry tend to cluster together in the diagram [35].

Principal component analysis method (PCA) and correlations are a popular method to assess groundwater quality. One of the principle advantages of multivariate techniques such as principal component analysis (PCA) is that they are able to rapidly reveal relationships between a large number of variables. In this study, PCA and correlations are used to identify the possible sources of major ions in groundwater, hydrogeological reactions that may occur in the study area, and dominant factors that control groundwater quality.

Gibbs diagrams which are a simple plot of the TDS versus the weight ratio of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ or $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$

FIGURE 4: Piezometric contour maps of the study area [31].

FIGURE 5: Location of sampled wells and piezometers in the study area.

are widely used to establish the relationships between the water composition and the lithological characteristics of the aquifer [36]. Three distinct fields, including precipitation dominance, evaporation dominance, and rock weathering dominance, constitute the segments in the Gibbs diagram.

Hydrogeochemical Modeling. The equilibrium state of the water with respect to a mineral phase can be determined by calculating saturation index (SI) using analytical data. In this study, saturation indices (SI) were calculated in terms of the following equation [37]:

$$SI = \log \left(\frac{IAP}{k_s(T)} \right), \quad (1)$$

where IAP is the relevant ion activity product, which can be calculated by multiplying the ion activity coefficient γ_i and the composition concentration m_i , and $k_s(T)$ is the equilibrium constant of the reaction considered at the sample temperature [35]. The geochemical modeling program PHREEQC has been used to evaluate the water chemistry.

SI > 0 indicates oversaturation and minerals may be subject to precipitation, SI < 0 means undersaturation and minerals will dissolve, and SI = 0 suggests saturation and minerals are in equilibrium status with respect to the solution [38].

4. Results and Discussion

4.1. Hydrogeochemical Characterization. Groundwater quality depends on various chemical constituents and their concentrations, which are mostly derived from the geological stratum of the particular region [6]. The pH was one of the primary indicators of the water chemistry evolution. The aquifer groundwater was neutral to slightly alkaline water, with a mean pH value of 7,23 and 7,15 in the wet and dry season, respectively. Electrical conductivity (EC) of the water samples was medium to high, suggestive of very highly mineralized waters. EC values ranged between 1240 and 6300 $\mu\text{S}/\text{cm}$ in the wet season and between 1131 and 5430 $\mu\text{S}/\text{cm}$ in the dry season. A problem to the water supply development in the area is the increasing electrical conductivity

TABLE 1: Chemical data of sampled wells and piezometers in the Ras Jbel aquifer.

Well	EC	pH	TDS	Wet season				Ca ²⁺	Mg ²⁺	Dry season				Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	EC	pH	TDS	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
				EC	pH	TDS	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻																	
1	3670	7.41	2369	225	89	443	225	89	443	10	999	298	305	299	140	757	12	1792	343	287	3670	7.41	2369	299	140	757	12	1792	343	287
2	3990	7.05	2519	447	57	413	447	57	413	4	1022	307	270	447	58	376	1	989	326	250	3990	7.05	2519	447	58	376	1	989	326	250
3	3840	6.8	2649	442	54	425	442	54	425	11	997	384	338	421	48	392	9	918	356	308	3840	6.8	2649	421	48	392	9	918	356	308
4	4120	7.1	3166	368	72	647	368	72	647	5	1021	742	311	327	63	506	2	789	626	299	4120	7.1	3166	327	63	506	2	789	626	299
5	6300	6.9	4110	520	89	738	520	89	738	7	1390	1005	361	501	94	731	4	1599	1040	354	6300	6.9	4110	501	94	731	4	1599	1040	354
6	5080	6.95	3345	403	81	666	403	81	666	8	1160	661	366	363	66	499	5	953	598	348	5080	6.95	3345	363	66	499	5	953	598	348
7	5790	6.9	3630	560	115	550	560	115	550	4	1457	635	309	523	103	471	3	1181	633	317	5790	6.9	3630	523	103	471	3	1181	633	317
8	3730	6.9	2306	286	115	284	286	115	284	20	895	377	329	353	135	294	12	876	421	317	3730	6.9	2306	353	135	294	12	876	421	317
9	5660	7.03	3800	368	129	881	368	129	881	11	1487	563	361	339	96	609	7	1248	498	329	5660	7.03	3800	339	96	609	7	1248	498	329
10	3530	7.3	2384	249	59	388	249	59	388	25	788	589	287	258	46	347	20	610	489	220	3530	7.3	2384	258	46	347	20	610	489	220
11	4480	7.12	3260	379	72	646	379	72	646	18	989	820	337	334	59	500	13	774	683	311	4480	7.12	3260	334	59	500	13	774	683	311
12	3250	7	2142	230	55	346	230	55	346	37	705	477	293	285	55	434	37	720	543	287	3250	7	2142	285	55	434	37	720	543	287
13	2770	7	1658	216	45	264	216	45	264	31	474	352	277	243	41	262	29	487	380	268	2770	7	1658	243	41	262	29	487	380	268
14	2480	7.65	1972	278	46	337	278	46	337	24	659	382	246	263	50	343	23	662	462	238	2480	7.65	1972	263	50	343	23	662	462	238
15	6250	7.96	4089	466	86	857	466	86	857	96	1463	811	310	353	71	605	26	866	684	445	6250	7.96	4089	353	71	605	26	866	684	445
16	4190	7.6	2480	258	78	444	258	78	444	22	830	619	231	276	70	421	19	766	598	244	4190	7.6	2480	276	70	421	19	766	598	244
17	3990	7.5	2715	274	49	550	274	49	550	107	775	460	500	280	50	426	80	652	413	598	3990	7.5	2715	280	50	426	80	652	413	598
18	2920	7.2	2046	221	56	330	221	56	330	79	472	444	445	199	45	289	75	444	363	427	2920	7.2	2046	199	45	289	75	444	363	427
19	2730	7.75	1817	236	54	285	236	54	285	25	451	382	381	215	46	256	31	427	395	311	2730	7.75	1817	215	46	256	31	427	395	311
20	4020	7.23	2747	208	131	525	208	131	525	6	1011	481	386	206	124	410	3	872	384	390	4020	7.23	2747	206	124	410	3	872	384	390
21	1240	7.78	819	48	36	165	48	36	165	7	289	102	173	104	57	270	5	639	108	134	1240	7.78	819	104	57	270	5	639	108	134
22	3280	7.05	2358	258	55	377	258	55	377	35	844	515	275	230	42	338	32	589	366	238	3280	7.05	2358	230	42	338	32	589	366	238
23	1573	7.68	924	84	19	200	84	19	200	6	276	89	250	73	12	182	3	217	88	207	1573	7.68	924	73	12	182	3	217	88	207
24	5170	7.15	2891	505	75	510	505	75	510	8	1185	407	201	490	67	433	5	1066	436	201	5170	7.15	2891	490	67	433	5	1066	436	201
25	4610	7.3	2910	189	113	576	189	113	576	7	916	652	458	211	123	590	4	878	650	433	4610	7.3	2910	211	123	590	4	878	650	433
26	5050	7.3	1938	255	65	287	255	65	287	27	594	415	296	216	55	270	12	464	264	387	5050	7.3	1938	216	55	270	12	464	264	387
27	3400	7.55	1662	178	48	289	178	48	289	87	478	356	226	257	62	312	35	568	371	323	3400	7.55	1662	257	62	312	35	568	371	323
28	3160	7.6	1662	178	48	289	178	48	289	87	478	356	226	279	57	280	16	593	393	293	3160	7.6	1662	279	57	280	16	593	393	293
29														187	66	419	6	713	587	198				187	66	419	6	713	587	198
30	3580	7.2	2353	199	80	437	199	80	437	11	819	613	195	205	72	427	11	732	582	189	3580	7.2	2353	205	72	427	11	732	582	189
31	3090	7.5	2187	225	71	394	225	71	394	10	710	560	217	228	68	424	7	766	637	201	3090	7.5	2187	228	68	424	7	766	637	201
32	3490	7.6	2317	231	69	479	231	69	479	10	749	560	221	269	80	572	7	866	723	287	3490	7.6	2317	269	80	572	7	866	723	287
33	4290	7.1	2886	358	70	404	358	70	404	20	954	729	351	454	90	654	23	1107	884	397	4290	7.1	2886	454	90	654	23	1107	884	397
34	3640	7.25	2648	292	66	520	292	66	520	15	851	591	315	305	67	401	12	764	575	305	3640	7.25	2648	305	67	401	12	764	575	305

TABLE I: Continued.

Well	EC	pH	TDS	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	EC	pH	TDS	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
						Wet season										Dry season				
35	3860	7.25	2836	326	81	550	27	874	634	344	3420	7.51	2487	304	71	455	14	756	571	317
36	4820	7.95	3253	398	81	472	36	1084	789	393	4110	7.43	3015	348	74	539	38	922	729	366
37	3740	7.45	2390	230	78	412	17	829	607	218	3320	7.32	2441	265	70	474	16	757	609	250
38	2720	7.7	1881	197	55	332	9	591	465	232	3650	7.5	2628	292	71	491	6	821	654	293
39	2080	7.7	1378	169	32	251	11	470	336	110	1817	7.49	1269	158	30	213	8	391	319	153
40	3540	7.4	2454	231	75	419	8	823	620	278	3770	7.19	2727	273	81	489	7	865	696	317
41	5030	7.1	3010	402	81	456	14	1166	689	201	3130	7.67	2233	232	68	431	7	734	578	183
42											2820	7.93	2061	179	65	371	6	683	580	177
44	2980	7.12	1817	236	43	324	78	531	337	270	2090	7.52	1694	198	42	234	64	502	355	299
45	2670	7.1	1694	215	43	277	69	493	316	281	2130	7.4	1553	203	40	258	67	437	294	256
46	2840	7.4	1741	200	55	267	9	555	375	281	3050	7.3	2277	285	69	390	3	770	516	244
47	3310	7.05	1749	300	59	217	3	680	233	256	3170	7.3	2257	389	57	249	2	807	522	232
48	4990	7.06	2856	555	82	400	5	1210	355	250	4120	7.1	2601	560	73	327	2	1084	372	183

EC ($\mu\text{S}/\text{cm}$); TDS, Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, SO₄²⁻, HCO₃⁻ (mg/l).

FIGURE 6: Spatial distribution of electrical conductivity (a) wet season and (b) dry season in Ras Jbel aquifer.

(EC) values of near-coastal shallow groundwater. The high EC of groundwater from wells located along the coast and in Bahirat Beni Ata can be explained by the seawater intrusion effect caused by the groundwater level drawdown due to overexploitation (Figures 6(a) and 6(b)).

Based on the conductivity values, the groundwater system could be classified into four groups: fresh water ($<500 \mu\text{S}/\text{cm}$), marginal water ($500\text{--}1,500 \mu\text{S}/\text{cm}$), brackish water ($1,500\text{--}5,000 \mu\text{S}/\text{cm}$), and saline water ($>5,000 \mu\text{S}/\text{cm}$). Based on our conductivity values it is evident that groundwater in Ras Jbel aquifer is in marginal and brackish waters. Few samples are of saline water type.

The study area is characterized by a wide range of salinities. Salinity values ranged between 500 and 3600 mg/l in the wet season and between 500 and 3500 mg/l in the dry season. The higher values of EC and salinity are indicators of higher ionic concentrations, probably due to the high anthropogenic

activities in the region and geological weathering conditions but also due to the intrusion of sea water into the groundwater system.

The relative content of a cation or an anion is defined as the percentage of the relative amount of that ion to the total cations or anions, respectively [39]. In the study area, the strong acid anions (Cl^- and SO_4^{2-}) exceed weak acid anions (HCO_3^- and CO_3^{2-}). On the other hand, sodium and calcium concentrations exceed magnesium and potassium contents. The triangular diagram (Figure 7) shows that the groundwater chemistry was mainly characterized by two groups. The first group was Cl^- - Na^+ type, in which Na^+ accounted for more than 52–65% of the total cations; the second group was Cl^- - $\text{Na}^+/\text{Ca}^{2+}$ type, in which Na^+ and Ca^{2+} accounted for 37–48% and 36–53% of the total cations, respectively. Chemical facies in the phreatic aquifer of Ras Jbel seem to be directly related to the configuration of the ante-quaternary

TABLE 3: Correlation matrix of dissolved species and the TDS for the study area in wet season.

	CE	TDS	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
CE	1									
TDS	0,98	1								
pH	-0,34	-0,32	1							
Ca ²⁺	0,84	0,83	-0,44	1						
Mg ²⁺	0,73	0,73	-0,30	0,43	1					
Na ⁺	0,84	0,87	-0,18	0,60	0,65	1				
K ⁺	-0,04	-0,05	0,23	-0,11	-0,28	0,01	1			
Cl ⁻	0,95	0,96	-0,37	0,84	0,76	0,84	-0,19	1		
SO ₄ ²⁻	0,73	0,76	-0,12	0,50	0,52	0,75	-0,02	0,65	1	
HCO ₃ ⁻	0,36	0,37	-0,20	0,20	0,37	0,42	0,30	0,27	0,32	1

FIGURE 8: Distribution map of the groundwater facies in the shallow aquifer of Ras Jbel.

and HCO₃ (Figure 10). It suggests carbonates weathering and pollution by fertilizer application.

In order to understand the origin of groundwater mineralization in Ras Jbel plain, the saturation index (SI) was calculated. The mineral facies are chosen based on the analysis result of groundwater quality, the main components of groundwater, and the occurrences conditions ([6, 43, 44]). In the study area, the main cations are Na⁺, Ca²⁺, and Mg²⁺ and the main anions are HCO₃⁻, SO₄²⁻, and Cl⁻; thus gypsum, anhydrite, calcite, dolomite, aragonite, and halite are chosen to be the mineral facies.

The positive values of the calculated SI with respect to calcite and dolomite for all groundwater samples (Figure 11) suggest their oversaturation in respect to these minerals (0,05 < SI_{calcite} < 1,32 and 0,08 < SI_{calcite} < 1,18 in the wet and dry seasons, resp., and -0,10 < SI_{dolomite} < 2,29 and 0,06 < SI_{dolomite} < 1,98 in the wet and dry seasons, resp.). As described by Appelo and Postma [45], the dissolution of calcite and dolomite is as follows:

Calcite:

Dolomite:

However, focusing on the scatter plots of bicarbonate versus calcium and calcium + magnesium versus bicarbonate we notice that groundwater samples are not plotted on the 1:1 straight lines of calcite and dolomite dissolution (Figures 12(a) and 12(b)). Groundwater samples show an excess of Ca²⁺ that can be explained by the gypsum dissolution.

The plot of SI_{Gypsum} and SI_{Anhydrite} versus TDS exhibits a proportional and parabolic shape evolution with negative values of the saturation indexes (Figure 11) (-1,86 < SI_{Gypsum} < -0,34 and -1,72 < SI_{Gypsum} < -0,35 in the wet and dry seasons, resp., and -2,08 < SI_{Anhydrite} < -0,56 and -1,94 < SI_{Anhydrite} < -0,56 in the wet and dry seasons, resp.). Thus, both calcium and sulphate are derived from the same origin, which is the dissolution of gypsum and anhydrite.

FIGURE 9: Spatial distribution of chlorides (a) wet season and (b) dry season in Ras Jbel aquifer.

However, the plot of sulphate versus calcium (Figure 12(c)) shows an excess of Ca^{2+} ions for the majority of the groundwater samples. For these samples, the $(\text{Ca}/(\text{Ca} + \text{SO}_4))$ ionic ratio greater than 0,5 ratio (from 0,53 and 0,79) confirms the ionic exchange process [46]. The $(\text{Ca}/(\text{Ca} + \text{SO}_4))$ ionic ratio close to 0,5 confirms that the main source of Ca^{2+} is the gypsum dissolution [46].

A bivariate diagram of sodium versus chloride (Figure 12(d)) reveals two main groups: for the first group halite dissolution was maintained for a slope equal to unity where majority of the samples are situated on the 1:1 straight of halite dissolution given by the following reactions [45]:

The second group includes the high-salinity samples (Na–Cl type), which do not follow the halite dissolution line and show

enrichment in chloride compared to sodium. Thus, another phenomenon other than geological effect is controlling their salinization, and this may be the salt water intrusion.

Water samples were plotted in the Gibbs diagrams, which takes into account the major role of natural mechanisms (rock weathering, evaporation, and precipitation). Figure 13 clearly shows that the mechanism controlling water chemistry seems to be a combination of the weathering of carbonates minerals as well as the evaporation-precipitation processes. However, low rates of the groundwater samples were obtained in areas that were dominated by rock-water interactions.

Samples with $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ or $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ ratios greater than 0,5 and TDS levels between 783 and 4323 mg/l showed that the groundwater chemistry was controlled mainly by the saline water mixing or evaporation. Evaporation results in increased TDS in relation to high ratios

FIGURE 10: Representation of variables into two principal factors: F1-F2 (a) and F1-F3 (b).

of dominant cations and anions and CaCO₃ precipitates by losing Ca²⁺ and HCO₃⁻.

4.2.2. Ionic Exchange Processes and Freshwater-Saline Water Mixing. Ion exchange is one of the important natural processes responsible for the concentration of ions in groundwater and has significant impact on the evolution of groundwater chemistry [18]. The dominance of salty groundwater dominated by sodium and chloride ions in Ras Jbel shallow aquifer provides evidence of mixing with an external salinity source, which could be the seawater from the coastal part of the aquifer. Cation exchange, responsible for the salinity signature, is described by two mixing mechanisms (freshening and saline water intrusion). Equations (6) and (7) show the gain

or loss related to Na⁺ and (Ca²⁺ + Mg²⁺) within the exchanger X.

The freshening process or direct ion exchange: where Ca²⁺ from freshwater displaced the marine cations Na⁺ and Mg²⁺ from the exchanger complex. The resulting loss of Ca²⁺ from solution decreases the saturation state for calcite and possibly causes calcite dissolution.

The intrusion of seawater or reverse ion exchange also triggered cation exchange reactions where Ca²⁺ was expelled from the exchanger by seawater Na⁺ and Mg²⁺. The released

FIGURE 11: Variation of saturation indices of selected minerals in wet and dry seasons.

Ca^{2+} is being flushed from the aquifer by groundwater flow [45, 47].

The plot of $[(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})]$ versus $(\text{Na}^+ - \text{Cl}^-)$ determines the exchange of Na^+ against $(\text{Ca}^{2+}$ or $\text{Mg}^{2+})$ through the clay matrix. The relationship $[(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})]$ is the gain or loss of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ due to the carbonates and gypsum dissolution. The relationship of $(\text{Na}^+ - \text{Cl}^-)$ determines the gain or loss of Na^+ relative to the halite dissolution. If there is no ion exchange, all water samples will be placed in the origin of diagram [46].

Figure 14 shows that reverse ion exchange is a dominant process. To confirm the effect of reverse ion exchange, chloroalkaline index CAI-1 was calculated in milliequivalents

per liter according to the relationship proposed by Schoeller [48]:

$$\text{CAI-1} = \frac{[\text{Cl}^- - (\text{Na}^+ + \text{K}^+)]}{\text{Cl}^-} \quad (8)$$

If reverse ion exchange occurs in groundwater, CAI-1 values are positive. The calculated CAI-1 values are positive for more than 70% of the water samples which confirmed that reverse ion exchange is a dominant process. This shows that the interaction between the seawater and groundwater in the study area is playing a major role in the contamination of the aquifer by seawater intrusion. These results indicate that seawater/freshwater interface is in a continuous evolution despite the artificial recharge operations since 1993, and this probably because of the permanent heavy pumping.

FIGURE 12: Water-rock interaction: relationships between different solutes of Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , and HCO_3^- (a, b, c, d).

Water samples concentrated in the origin of the plot $[(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})]$ versus $(\text{Na}^+ - \text{Cl}^-)$ indicated the absence of the ion exchange process which can be attributed to the evaporation process followed by carbonate precipitation [49]. This result confirmed the results obtained using saturation states of minerals and Gibbs diagrams.

The seawater fraction in the groundwater is often estimated using chloride concentration [50]. Chloride ion has

been considered as a conservative tracer not affected by ion exchange [51]. For conservative mass balance of the mixture, the equation used is as follows [45]:

$$f = \frac{(\text{Cl}_{\text{mix}} - \text{Cl}_{\text{freshwater}})}{(\text{Cl}_{\text{seawater}} - \text{Cl}_{\text{freshwater}})} \times 100, \quad (9)$$

where Cl_{mix} is the Cl^- concentration of the sample, $\text{Cl}_{\text{seawater}}$ is the Cl^- concentration of the Mediterranean Sea, and

FIGURE 13: Gibbs diagram showing TDS versus (a) $\text{Na}/(\text{Na} + \text{Ca})$ and (b) $\text{Cl}/(\text{Cl} + \text{HCO}_3^-)$.

FIGURE 14: Plot of $[(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})]$ versus $(\text{Na}^+ + \text{K}^+ - \text{Cl}^-)$ for ion exchange.

$\text{Cl}_{\text{freshwater}}$ represents the Cl^- concentration of the fresh water. The fresh water sample will be chosen considering the lowest measured value of the electrical conductivity.

The rate of mixture varies from 0,32% (well n°23) in the north of the Raf Raf region and where the configuration of the ante-quaternary substratum prevents the marine intrusion to 13% (well n°1) near the shoreline (close to the coast). The highest value of the mixing fraction corresponds to the highest measured values of Cl^- and EC (1792 mg/l and 5430 $\mu\text{S}/\text{cm}$, resp.).

4.3. Isotopes and Groundwater Origin. The stable isotope ratios of oxygen and hydrogen in the groundwater are useful tools to differentiate between salinity origins [52, 53] and to help us understand various sources of recharge processes to groundwater because they are sensitive to physical processes such as atmospheric circulation, groundwater mixing, and evaporation ([33, 54]).

In arid and semiarid regions evaporation could be an important process influencing groundwater chemistry [19]. To understand the relationship between isotopic composition of groundwater of the shallow aquifer of Ras Jbel and those of precipitation measured at the station of Tunis Carthage situated at 50 km from the plain of Metline-Ras Jbel- Raf Raf, a bivariate diagram $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ is plotted in Figure 15(a).

A local meteoric water line (LMWL) for Tunis Carthage was used to interpret the data in this study. The local meteoric water line (LMWL) is controlled by local hydrometeorological factors, including the origin of the vapor mass, reevaporation during rainfall, and the seasonality of precipitation [33]. The isotope composition of the precipitation was plotted along the LMWL using the following equation: $\delta^2\text{H} (\text{‰}) = 8 * \delta^{18}\text{O} (\text{‰}) + 12,4$ (which had a correlation coefficient $R^2 = 0,99$) [55, 56].

Figure 15(a) shows that the isotopic composition of most of the groundwater samples collected in the wet season (except for sampling site number 35) lies within a narrow range, confirming that these groundwater samples had the same recharge source. Furthermore, all groundwater samples are scattered around the LMWL indicating that the recharge of the Ras Jbel shallow aquifer originates from infiltration of recent precipitation from Mediterranean vapor masses. Based on their isotopic composition, two groups of groundwater samples were identified (Table 4). The first group is relatively depleted in isotopic values and includes samples with $\delta^{18}\text{O}$

FIGURE 15: Isotopic relationships of groundwater in the study area.

and $\delta^2\text{H}$ values ranging from $-6,03$ to $-5,37\%$ versus V-SMOW and from $-33,94$ to $-29,66\%$ versus V-SMOW, respectively. This may be explained by the fact that nonevaporated water is rapidly infiltrated to the saturated zone.

As per the second group, values vary from $-5,35$ to $-3,50\%$ versus V-SMOW and from $-29,37$ to $-22,15\%$ versus

V-SMOW, for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. The relatively enriched isotopic values of the group 2 samples demonstrate that this groundwater is affected by evaporated open water or soil water.

The groundwater samples collected in the dry season were enriched compared to those collected in the wet season. The

TABLE 4: Isotopic data of sampled wells and piezometers in Ras Jbel aquifer.

Parameters	$\delta^{18}\text{O}$ (‰ versus SMOW)	$\delta^2\text{H}$ (‰ versus SMOW)	$\delta^{18}\text{O}$ (‰ versus SMOW)	$\delta^2\text{H}$ (‰ versus SMOW)
	Wet season		Dry season	
Minimum	-6,03	-33,94	-5,74	-31,46
Maximum	-3,5	-22,15	-0,06	-10,31
Average	-4,91	-28,06	-3,78	-23,33

results show isotopic content ranging from $-5,74$ to $-0,06\text{‰}$ versus V-SMOW for $\delta^{18}\text{O}$ and from $-31,46$ to $-10,31\text{‰}$ versus V-SMOW for $\delta^2\text{H}$. This may be explained by heavy isotope enrichment in the groundwater caused by strong evaporation given that there was effectively no precipitation in the study area between the two sampling periods; meanwhile, the groundwater may have been mainly recharged by lateral inflow from outside the study area, resulting in seasonal fluctuations in the isotopic values. The enriched groundwater samples (n°15, 20, 25, 30, 32, 35, 38, 41, 45, and 48) might be an indicator for evaporation of the recharge water before its infiltration to the aquifer.

The isotopic data for the groundwater collected in the wet season were linearly fit using the regression equation $\delta^2\text{H} (\text{‰}) = 4,01 * \delta^{18}\text{O} (\text{‰}) - 8,37$ ($R^2 = 0,82$). This regression line can be interpreted as the groundwater evaporation line (GEL). The gel has a $\delta^2\text{H}/\delta^{18}\text{O}$ slope <8 , which reflects evaporation during or after rainfall and/or mixing with an external water source (e.g., return of irrigation water) with high $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values. Furthermore, the GEL of the wet season intersected the LMWL at values of $\delta^{18}\text{O} = -5,22\text{‰}$ versus V-SMOW and $\delta^2\text{H} = -29,37\text{‰}$ versus V-SMOW. These values are estimated as baseline for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in recharging rainfall (Figures 15(b) and 15(c)). If samples are plotted above the lines, significant groundwater evaporation process can be confirmed.

Additionally, the isotopic data from the dry season were linearly fit using the regression equation $\delta^2\text{H} (\text{‰}) = 3,09 * \delta^{18}\text{O} (\text{‰}) - 11,81$ (with a correlation coefficient $R^2 = 0,83$). The GEL has a smaller slope than the LMWL, because evaporation tends to enrich heavy isotopes in water ([19, 57]). The increase in groundwater salinity due to evaporation can thus result in simultaneous increase in heavy isotopes ([19, 35]). The GEL of the dry season intersects the LMWL at values of $\delta^{18}\text{O} = -4,93\text{‰}$ versus V-SMOW and $\delta^2\text{H} = -27,32\text{‰}$ versus V-SMOW, which are chosen as baselines (Figures 15(d) and 15(e)). It is observed that 80% of the groundwater samples were plotted above the baselines and this demonstrates that evaporation has a significant contribution to groundwater salinity in the study area.

Furthermore, the deuterium excess calculated as d-excess $= \delta^2\text{H} - 8\delta^{18}\text{O}$ [54] has been widely used in hydrological studies. The d-excess is used to identify secondary processes that influence the atmospheric vapor content in the evaporation-condensation cycle in nature ([54, 58]). The d-excess plotted against $\delta^{18}\text{O}$ shows a negative correlation for the whole set of samples (Figure 16). The decrease in d-excess

FIGURE 16: Plot of d-excess versus $\delta^{18}\text{O}$.

is an indication that evaporation has occurred during the recharge process which again confirms the previous results.

4.4. Irrigation Return Flow. Irrigation return flow is defined as the excess of irrigation water that is not evapotranspired or evacuated by direct surface drainage and which returns to an aquifer or surface water [59, 60]. Irrigation return flows may induce salt and nitrate pollution of receiving water bodies [61]. Indeed, NO_3^- is the most common water contaminant, and NO_3^- pollution is increasing because the number of anthropogenic sources is increasing [26].

71% of groundwater samples are contaminated by nitrates where the concentration exceeds the permissible value of 50 mg/l set by WHO [62]. The spatial distribution of nitrates (Figure 17) shows that high nitrate contents are observed especially in the upstream of Ras Jbel aquifer. Groundwater contamination by nitrate is due to the intensive use of nitrogen fertilizers ($\text{Ca}(\text{NO}_3)_2$, KNO_3 , and MgSO_4). In recent years, the agricultural land area in Ras Jbel plain has increased and copious amounts of nitrogenous fertilizer have been used, which have increased the groundwater NO_3^- concentrations.

Furthermore, return flow from irrigation water also seems to contribute notably to the recharge process. Most of groundwater samples shows a correlation between NO_3^- and $\delta^{18}\text{O}$, reflecting the significant role of evaporated and contaminated irrigation water to the groundwater salinization (Figure 18(a)). Huge quantities of irrigation return flow

FIGURE 17: Spatial distribution of nitrate concentrations in the shallow aquifer of Ras Jbel during the dry season.

FIGURE 18: Plots of NO_3^- versus water table depth and $\delta^{18}\text{O}$ versus NO_3^- .

elevated groundwater level, hence increasing evaporation and inducing salinization [63]. As highlighted in Figure 18(b), the contamination by return of irrigation water is observed in the shallower horizons (depth ≤ 13 m).

5. Conclusions

This paper aimed to discuss the origin, processes, and mechanisms of groundwater salinization, as well as the chemical evolution of groundwater in the Ras Jbel coastal aquifer using isotopic tools and hydrochemical tracers.

Most of the groundwater is considered to be of brackish to saline water and contains high ion concentrations. The groundwater in the study area is influenced by both natural and anthropogenic factors. The major geochemical processes controlling hydrochemical evolution are the inverse cationic exchange due to the phenomena of seawater intrusion, dissolution of evaporates minerals (halite, gypsum, and/or anhydrite), irrigation return flow, water-rock interactions, and

evapo(transpi)ration. (Figure 19). The mixing rate among freshwater and saline water ranges between 1 and 13%.

In addition, groundwater in the shallow aquifer of Ras Jbel is also contaminated by agricultural fertilizers containing high amounts of nitrates. Nitrates are transported to the aquifer by natural recharge process and by return flow from irrigation water.

Hydrogen and oxygen-18 stable isotopes signatures of groundwater have identified recent groundwater recharge by infiltration of local precipitations. The enrichment in stable isotope of groundwater confirms that return flow of irrigation waters is an important factor influencing groundwater quality.

The results of this study can be used to improve our understanding of hydrogeochemical processes and enable the protection and sustainable use of water resources. It, therefore, calls for more comprehensive research for better water resources management.

FIGURE 19: Schematic conceptual model summarizing salinization sources of groundwater in the plain of Ras Jbel.

Conflicts of Interest

The authors declare no conflicts of interest.

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