

GROUNDWATER SALINITY IN THE KHABOUR-EUPHRATES DOWN-STREAMS VALLEYS

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Abstract

The Euphrates river water and groundwater in the lower part of the Euphrates and Khabour river valleys, in eastern Syria, have been studied using hydrochemical and environmental isotope methods to assess the hydrogeological features of this system, and then to characterize the dynamic of groundwater salinization in this sector. The Euphrates river water, which was rather fresh (TDS < 0.7 g/L) and has slightly increased in its salinity levels during the last two decades, was generally of a calcium-sodium, sulphate-bicarbonate-chloride type. Groundwaters, which were originated from the Euphrates river by a direct lateral inflow, together with a vertical percolation of irrigation water, differ chemically from that of the Euphrates water, mainly in terms of salinity contents and by their evolution pattern towards a sodium-chloride type. This evolution reflects the important role of the evaporation process in this dry region, and it agrees with the results of the thermodynamic geochemistry simulation tests based on evaporation of the Euphrates river water. Groundwater salinity could be formed as a result of dissolution of halite and thenardite minerals, largely detected in considerable amounts on the soil surface. Stable isotopes permit a distinction between three groups of waters: 1) groundwater affected by high and slow evaporation processes; 2) groundwater affected by low evaporation process, and 3) groundwater affected by intermediate evaporation process. Relationships between stable isotopes and major ions permit a distinction between two processes that increase the salinity: 1) enrichment by evaporation only; and 2) enrichment by both evaporation and dissolution of salts. The absence of a working drainage system, together with irrigation under high evaporation rates and low depths of the water table, are the primary reasons for the continuous deterioration of groundwater quality and the accumulation of salts in the soils of the study area.

Keywords: hydrology, environmental isotopes, salinization, groundwater, Syria

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Introduction

Salinization of groundwaters and soils is one of the serious problems in hydrogeology. This problem can in fact limit the development of agricultural programs, and thus it may have a negative influence on the economy sector. Saline groundwater was already observed long ago, as a common phenomenon in arid and semi-arid regions, where the effective natural flushing of accumulated salts was relatively absent (Drever, 1977). Groundwater salinity may also be the result of several factors: 1) sea water intrusion; 2) migration of saline water (from dissolution of salts) and its mixing with fresh water; 3) infiltration of polluted saline water (from agricultural activities) towards the groundwater (Hem, 1992; Vengosh and Rosenthal, 1994). Also, water salinity could be due to a high evaporation rate (Droubi, 1976; Gac, 1980).

The ongoing salinization of soils and groundwater in the lower part of the Euphrates and Khabour river valleys (Figure 1) is one of the major problems in Syria. This phenomenon was the subject of some earlier hydrodynamic and geochemical investigations (Dosso et al., 1976; GERSAR-SCET, 1977; Dosso, 1980). Based on a hydrodynamic model, the evaporation rate from the groundwater table was estimated to attain 10 % of total irrigation amount. Geochemical simulation predicts the precipitation of several minerals (calcite, Mg-montmorillonite, magnesite, gypsum, thenardite and sylvite) during the evaporation of Euphrates water. Accordingly, it was recommended to drill several drainage wells in the area to drain the saline shallow water into the Euphrates river, and a network of drainage wells was established, and several wells still work up to date.

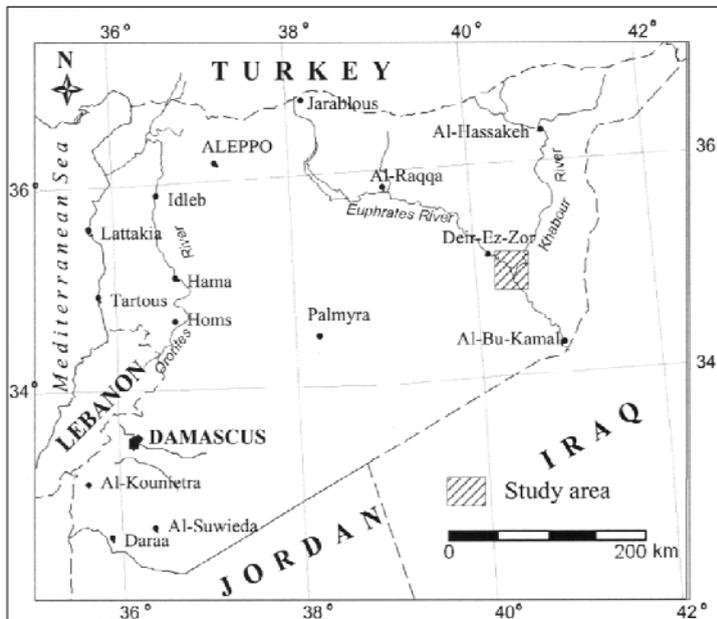


Figure 1. Location map showing the study area.

This work, which was initiated within the frame work of the IAEA regional T/C project entitled "Isotope application for improved groundwater utilization (RAW/8/007)", aims to apply environmental isotope

methods, together with hydrochemistry, to review and assess the dynamics of the salinization processes of groundwater in the lower part of the Euphrates-Khabour rivers valleys. This research may also represent a contribution to define a proper and a suitable management strategy that can help to minimize the salinization of soil and groundwater, and save the fertility of cultivable lands in this part of the country.

General characteristics of the study area

The selected area for this specific study is located in the eastern part of Syria (Figure 1). It covers a band of land of about 10 km on the right bank of the Euphrates river, from Deir-Ez-Zor to Al-Mayadine. Also, it includes some lands on the left bank of the Khabour (main affluent of the Euphrates) and the Euphrates rivers. The topography of the area is simple and generally dominated by flat lands (190-200 m.a.s.l.), expanded along the two banks of the Euphrates river valley, and by the presence of some rocky cliffs (up to 230 m) on the right bank of the Euphrates river.

The climate is of a desert type, and thus the study area is characterized by its aridity. The mean monthly air temperature varies between 8 °C (December and January) and 33 °C (July and August), with a possibility to reach 48 °C during August. The mean annual air temperature oscillates around 20 °C, with a gradual increase from north to south (UNDP-FAO, 1966; Dosso, 1980). The amount of precipitation is among the lowest values in the country. The average long-term precipitation varies between 161 mm/a in Deir-Ez-Zor and 129 mm/a in Al-Bu-Kamal. The mean monthly value of relative air humidity ranges between 24-27 % (June to August) and 70-75 % (December and January). The mean annual value of relative air humidity in the area (44-47 %) is among the lowest registered values in the country. The mean monthly evapotranspiration value varies from 31 mm (December) to 417 mm (July), with a mean annual value of about 2113 mm (Dosso, 1980).

Flood irrigation is currently practiced to irrigate the flat alluvium land along the edges of the Euphrates. Waters from this river are mainly used throughout series of small-uncovered canals or pipelines, directly connected with pumps close to the river course. The cultivated lands are mainly planted with cereal crops (wheat and barley) in winter, and with cotton and maize in summer. Consequently, the water table reaches its maximum at the end of April, which is the period of maximum irrigation and lowest evaporation rate. The annual inflow to the water table has been assumed 30 % of the irrigation water volume.

Geology and hydrogeology

The study area belongs to the stable part of the Arabian platform. It occupies the central part of the so-called "Deir-Ez-Zor depression". According to Ponikarov (1967), this area is stratigraphically characterized by the exposures of Neogene and Quaternary deposits (Figure 2).

The Neogene deposits (total thickness of about 220 m) are outcropping within the Deir-Ez-Zor depression. They are represented by gypsum, silty clays, sandstones and with shelly beds, sandstones, siltstones and clays in the lower part; and sands, siltstones marls, gypsum, sandstones and pebbles in the upper part.

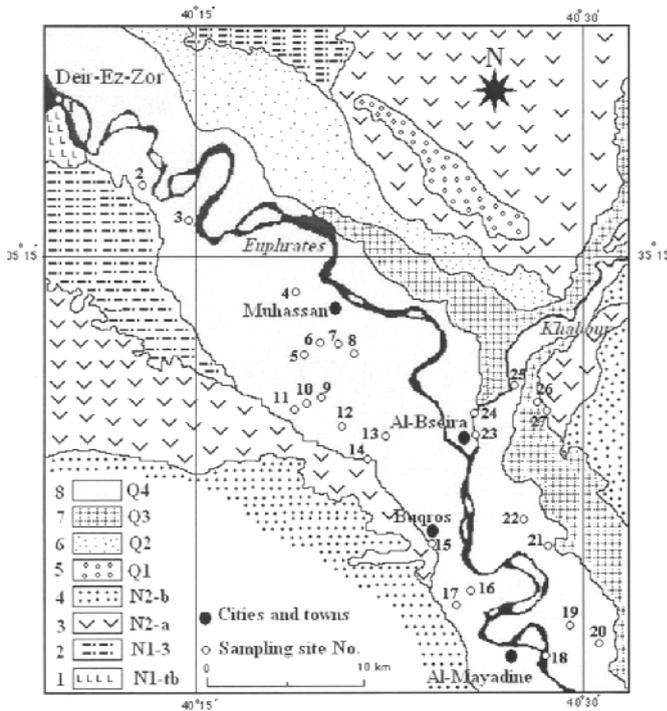


Figure 2. Geological map of the study area showing the selected sampling sites.

1: Middle Miocene; 2: Upper Miocene; 3: Lower Pliocene; 4: Upper Pliocene; 5: Lower Quaternary; 6: Middle Quaternary; 7: Upper Quaternary; 8: Recent Quaternary.

The Quaternary deposits (total thickness of about 20 m) are represented by cross-bedded pebbles of Lower (Q1) and Middle (Q2) Quaternary ages, which are developed in all the terraces of the Euphrates and Khabour rivers. Some effusive volcanic (basaltic) rocks of Lower Quaternary age can also be seen in the vicinity of the study area. The deposits of the Upper Quaternary (Q3) are also widely developed in the river valleys, and are composed of alluvial deposits (pebbles, gravels, loams and sandy loams). The Recent Series of Pleistocene and Recent (Q4) deposits (thickness of less than 0.5 m) are made up of gravels and loams with a thin gypsiferous crust.

X-rays of sub-soil samples show the presence of calcite. This is not surprising considering the nature of alluvial deposits. Although the alluvial deposits of the Euphrates contain much less gypsum, this mineral could be also found in high amounts in form of crystals in the Neogene deposits. Gypsum and anhydrite are the major salts, which are more abundant near the cliff and the upper profile than near the Euphrates. They are associated with other minerals such as: mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10(\text{H}_2\text{O})$), thenardite (Na_2SO_4) and bloedite ($\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4(\text{H}_2\text{O})$). Thus, the most soluble salts, which seem systematically distributed near the top of the profile, are mostly dissolved in the capillary retention water. This is the result of successive inflow of irrigation water, which dilutes the waters previously concentrated in the upper profile through evapo-transpiration.

The hydrogeological feature of the study area is highly influenced by the presence of three main aquifer systems (GERSAR-SCET, 1977):

- *The water-bearing system of the deep Miocene*: this aquifer seems to be not connected with the upper two alluvial aquifers, developed in the Euphrates and Khabour valleys.
- *The water-bearing system of the Miocene-Pliocene complex*: this reservoir is characterized by the existence of two series: 1) the rather fractured formation of marl and gypsum; and 2) the alluvial formation expanded along the river valleys.
- *The water-bearing system of the Euphrates-Khabour alluvial*: this aquifer is generally composed of gravels and pebbles of bigger size at the bottom, and finer alluvial sediments (loams and sandy loams) at the top, and it is laterally connected with the water-bearing system of the Miocene-Pliocene complex. As a result of the rather important vertical change in particle size, and intercede, there is a vertical difference in the permeability values. Also, the existence of a compact to semi-compact layer at the bottom enhances recharge and irrigation waters to move vertically in the upper part, and then horizontally -towards the river- in the lower part (Figure 3).

This mechanism of groundwater flow could be explained by the hypothesis that, during the irrigation period, the amount of vertically penetrated water exceeds the quantity of drained groundwater towards the river, rising consequently the water table (GERSAR-SCET, 1977; Dosso, 1980). While, a part of the water is stored in the fine alluvium layer, another fraction of water is lost by evaporation through capillary movement, directly from the water table (2-4 m below the earth's surface). This phenomenon could be considered as the primary cause for the salinization of soil and groundwater in the Euphrates valley. Figure 4 shows the piezometric map of the groundwater table in the study area during May 2000. According to this map it can be observed that groundwater movement is mainly from the north-west towards the south-east, which clearly agrees with the water flow in the Euphrates river.

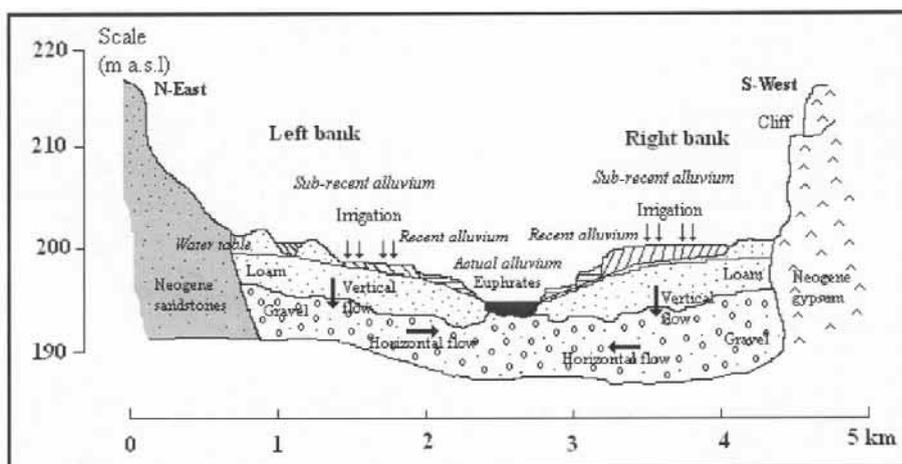


Figure 3. Schematic cross-section of the Lower Euphrates valley.

Sampling and analytical methods

Several campaigns were undertaken in the study area from January 2000 to October 2001. Seventy-five water samples were periodically collected from 27 different sites during the rainy (January-April) and the dry seasons. Twenty-two sites correspond to shallow wells (20-50 m), and the remaining five sites were selected on the Euphrates and Khabour river courses.

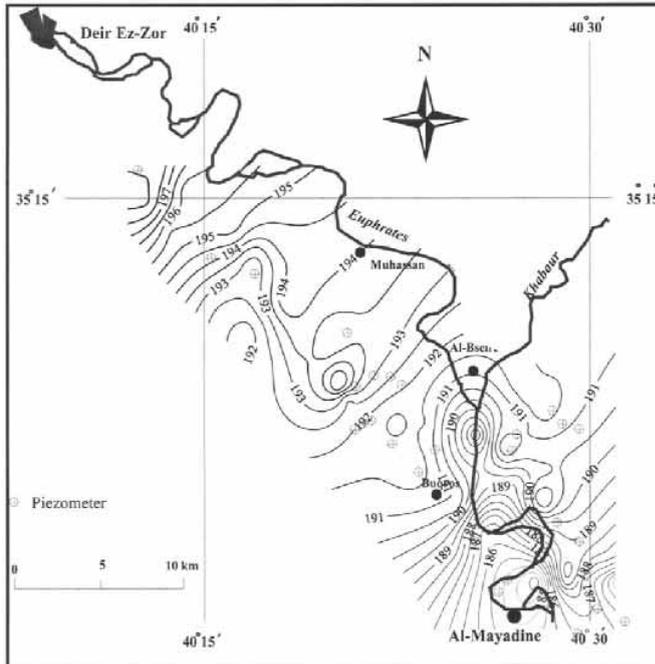


Figure 4. Spatial distribution of the piezometers and water table (m a.s.l.) of the groundwater in the study area during May 2000.

Water samples were collected in four rinsed plastic bottles. A small bottle of 50 mL was taken for the determination of stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$), and the related analyses were performed by means of a mass spectrometer in the PINSTECH isotope laboratory of Pakistan. A bottle of one liter 1 L was collected for tritium measurement, and the analyses of this isotope were performed (after electrolysis) in the Geology Department of the Syrian Atomic Energy Commission (SAEC), using a liquid scintillation counter. Measurement accuracy for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ and tritium are ± 0.1 , ± 1.0 ‰, and ± 1 TU, respectively.

A 0.5 L bottle was filled and acidified for the determination of major cations (Ca^{++} , Mg^{++} , Na^+ and K^+). These analyses were performed by the atomic absorption method at the chemistry laboratories of SAEC. The last 0.5 L bottle was taken for the major anions (Cl^- , SO_4^{2-} and NO_3^-), and the related analyses were carried out by liquid chromatography (HPLC), after passing the water samples through a $0.45 \mu\text{m}$ filter in the chemistry laboratories of SAEC. Temperature, pH, electrical conductivity (E.C) and total alkalinity (i.e. HCO_3^-) of water samples were determined in the field. Furthermore, six soil samples were collected from the earth's surface for mineralogical determination, and the related X rays analyses were carried out in the Geology Department of SAEC.

Results and discussion

Chemistry of the Euphrates river water

Table 1 compiles the mean hydrochemical and isotopic data for the selected sites in the study area during the period 2000-2001. The Euphrates river water at Deir-Ez-Zor site was rather fresh (total dissolved solids TDS < 600 ± 150 mg/L), and it becomes slightly more saline (685 ± 200 mg/L) at Al-Mayadine site. As a result of evaporation and seepage of saline waters in the Euphrates river, the concentrations of sodium, calcium, chloride and sulphate were more pronounced at Al-Mayadine site compared with those at Deir-Ez-Zor. The pH value of the Euphrates river water stays around 8.5 ± 0.2 at these two sites, while the water temperature increases about 1 °C at Al-Mayadine site. The chemistry of the Euphrates river water was slightly changed since 1976, probably because of changes of the river water quality in the Turkish side. At that time, the TDS content was in the range from 0.4 to 0.7 g/L (Dosso, 1980). The water chemistry of the Euphrates river is generally characterized by a calcium-sodium and sulphate-bicarbonate-chloride type, with the following ionic sequences: Ca²⁺>Na⁺>Mg²⁺>K⁺ and SO₄²⁻>HCO₃⁻>Cl⁻.

Table 1. Mean hydrochemical and isotopic data of water samples collected from the study area.

Site Nº.	Location	pH	T	E.C.	Na ⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	TDS	δ ¹⁸ O	δ ¹⁸ H	d	³ H
			°C	µS/cm	mg/L							(‰, V-SMOW)		(TU)
1	E1 (5)*	8.53	18.1	783	71.4	87.6	78.9	172	164	597	-7.26	-50.2	7.9	9.3
2	W293 (2)	7.19	22.3	653	1165	661	1127	3617	332	7299	-7.24	-49.5	8.4	10.9
3	WP1 (2)	7.63	20.8	3865	457	390	647	1160	382	3246	-7.22	-49.9	7.9	10.0
4	WP2 (1)	7.68	21.0	3220	174	240	327	682	257	1789	-7.13	-50.5	6.5	11.1
5	W1050 (1)	9.02	13.3	3560	412	200	527	1384	218	2933	-6.22	-47.1	2.7	11.4
6	W1053 (1)	7.64	21.0	8950	1568	400	1812	3387	347	8019	-7.39	-51.9	7.2	9.9
7	W2003 (1)	8.20	21.4	6480	1119	240	1344	2240	284	5611	-7.39	-49.9	9.2	11.0
8	W166 (1)	8.00	21.4	7070	1108	360	1109	1995	305	5229	-7.35	-49.1	9.7	9.7
9	W1188 (1)	8.47	15.4	3995	497	480	710	1480	241	3589	-6.09	-43.6	5.1	9.9
10	W1187 (2)	7.36	20.5	6690	1389	283	1287	1959	415	5559	-7.11	-50.7	6.2	10.6
11	W157 (1)	7.39	22.9	24850	7664	960	6279	8587	290	24558	-6.35	-49.1	1.6	8.5
12	W299 (1)	7.53	22.2	23595	6449	808	6871	6345	233	21668	-6.76	-49.1	5.0	7.0
13	W443 (1)	7.92	21.6	22275	5546	640	6490	5647	263	19455	-7.19	-51.6	5.9	10.0
14	W439 (1)	7.32	22.3	37093	8367	800	9129	8700	316	28811	-5.93	-45.8	1.7	4.5
15	W830 (2)	7.40	21.4	6733	876	615	950	2826	283	6077	-6.74	-45.8	8.2	9.6
16	WP3 (2)	7.56	20.8	4557	514	372	828	1819	333	4196	-7.38	-51.5	7.6	10.4
17	W23 (2)	7.78	21.1	4580	646	302	676	1694	313	3910	-7.36	-52.1	6.8	10.4
18	E2 (4)	8.57	19.3	848	85.3	104	89.5	217	163	685	-7.28	-51.4	6.8	9.6
19	WP4 (2)	7.45	20.8	3838	347	299	475	1281	374	2978	-7.46	-51.6	8.1	11.4
20	W3511 (3)	7.36	21.1	7677	987	685	1524	2730	378	6856	-7.34	-51.5	7.3	10.3
21	W2213 (1)	7.25	20.6	2120	232	199	280	445	329	1596	-7.42	-50.9	8.5	9.7
22	W1813 (2)	7.57	18.6	4750	600	520	594	2293	305	4609	-7.10	-49.4	7.4	9.0
23	K1 (2)	8.07	17.3	949	120	122	112	308	207	906	-7.46	-50.8	8.9	9.2
24	K2 (2)	7.95	17.5	2099	369	222	568	1008	264	2576	-7.29	-51.4	6.8	9.3
25	K3 (3)	7.71	19.6	4310	560	425	758	1595	296	3876	-5.99	-43.1	4.7	8.2
26	WP5 (2)	7.11	22.4	5270	697	780	1365	1845	314	5334	-4.53	-32.4	3.9	5.1
27	WP6 (1)	7.13	21.9	8105	1422	1200	2661	2099	171	8237	-4.26	-29.3	4.7	4.1

*: Numbers between brackets indicates the number of analyzed samples.

As the Khabour river was effectively dry during the study period, the water chemistry along its course reflects rather an admixture between groundwater and the Euphrates river water. On the basis of major ion concentrations, the calculated optimized mixing ratios between the Euphrates river water (Deir-Ez-Zor site) and groundwater (site no. 27), show that the contribution of the Euphrates river water was about 96%, 74% and 58%, for the sites nos. 23, 24 and 25, respectively.

Chemistry of groundwater

The average groundwater temperature ranges between 13.3 °C and 22.9 °C, but the majority of the sampled sites have temperature values above 20 °C. The average pH value of groundwater ranges between 7.13 and 9.02. The value of electrical conductivity (E.C.) of groundwater is generally high and exceeds 2 mS/cm. This value ranges between 2.12 μ mS/cm, near the Euphrates river course, and 37.1 mS/cm (site no. 14). The spatial distribution of the groundwater E.C. value in the study area (Figure 5) is represented by a gradual decrease towards the river course, most probably as a result of mixing process with the Euphrates river water. Similarly, the spatial distribution of Na^+ (Figure 6), Cl^- , SO_4^{2-} and TDS contents follows the pattern of E.C. variations. However, few exceptions were reported for Ca^{2+} , Mg^{2+} and HCO_3^- patterns. These ions largely differ in terms of spatial variation from those of the other major ions. The relationship between the major ion concentrations and TDS content (Figure 7) reveals that the salinization of groundwater was due to three species: Na^+ , Cl^- and SO_4^{2-} , which tend to increase linearly with the increasing value of TDS. The concentrations of Ca^{2+} , Mg^{2+} and HCO_3^- species, which could be controlled by the precipitation of calcite, magnesite and Mg-clay minerals, stay rather constant with the increasing TDS content. In fact, the precipitation of these minerals consumes, in the earlier stages of evaporation, large amounts of the above-mentioned ions. Whereas, the remaining ions (Na^+ , K^+ , Cl^- and SO_4^{2-}) in the solution, which can contribute to form halite (NaCl), thenardite (Na_2SO_4), and sylvite (KCl) minerals, are thermodynamically supposed to be precipitated at higher degrees of evaporation or very high concentration values (Droubi, 1976; Gac, 1980; Stumm and Morgan, 1981).

The mechanism that controls this geochemical behavior can be explained by the fact that during carbonate and gypsum precipitation there are no important precipitation reactions that can maintain low sodium and potassium concentrations in water (Hem, 1992). In parallel, as the concentration of both sodium and potassium is high enough than those of magnesium and calcium, cation exchange interactions in groundwater systems tend to extract divalent ions (i.e. Ca^{2+} and Mg^{2+}) from the solution and replace them with monovalent ions, such as Na^+ and K^+ (Stumm and Morgan, 1981; Hem, 1992).

The spatial distribution pattern for most of the major ion concentrations could be explained by the interference of three main factors: 1) the Euphrates river, which plays an essential role in diluting their concentrations; 2) the groundwater movement, which favors the dissolution of evaporite rocks (gypsum), widely contained in the Lower Pliocene substratum; and 3) the evaporation processes, which could also increase the concentration of major ions.

Figure 8 represents a projection of the chemical composition of the water sample points in the Piper diagram. This diagram permits the distinction between three main groups: 1) the relatively fresh waters of the Euphrates river and the surrounded wells (site no. 21), which tend to have a similar chemical type (calcium-sodium and sulphate-bicarbonate-chloride type); 2) the saline groundwater (sites nos. 10-14),

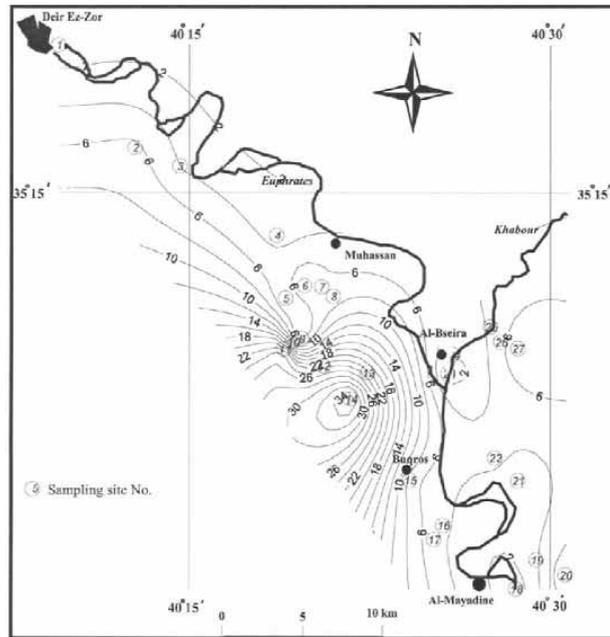


Figure 5. Spatial distribution of the electrical conductivity value (mS/cm) of the groundwater in the study area during 2000-2001.

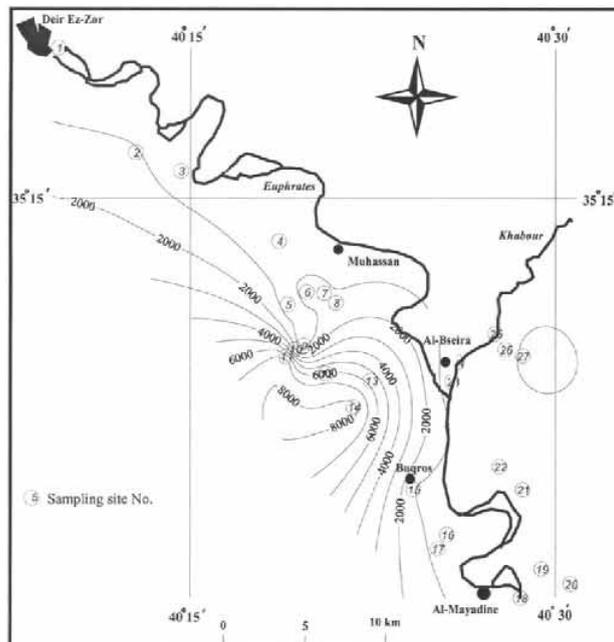


Figure 6. Spatial distribution of the sodium concentration (mg/L) of the groundwater in the study area during 2000-2001.

which tends to have a sodium and chloride-sulphate type (rather similar to that of seawater); and 3) the admixed groundwater of the remaining sites, which shows an intermediate chemical type between the above two groups.

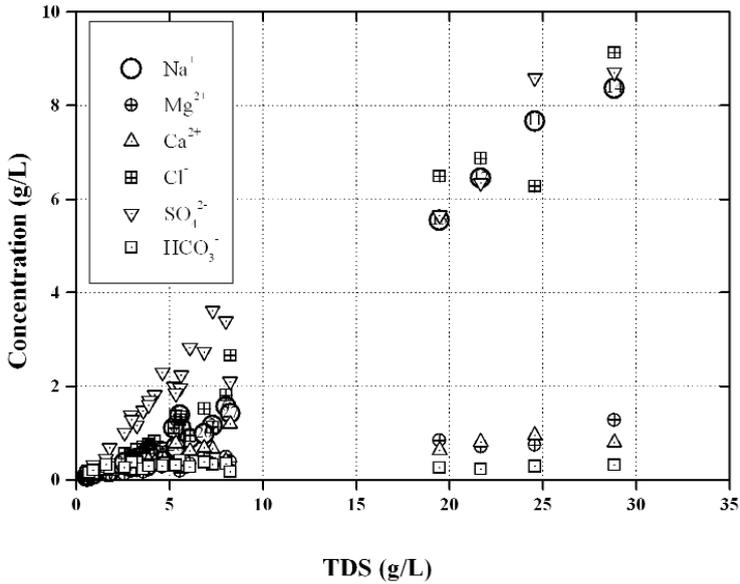


Figure 7. Relationship between major ion concentrations and TDS of the water in the study area during 2000-2001.

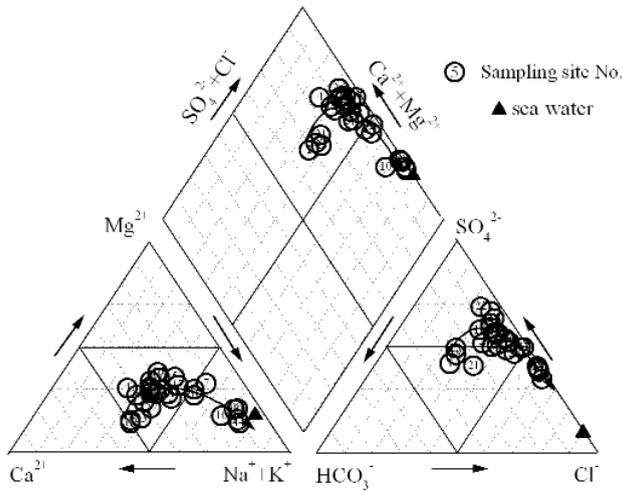


Figure 8. Piper diagram of the chemical composition of water samples collected from the study area during 2000-2001.

The chemical evolution of groundwater in the study area is identical to the evolution already obtained by Dosso (1980), by adopting a thermodynamic simulation, based on a progressive evaporation of the Euphrates river water (Figure 9). Results of this simulation show that the evaporated water of the Euphrates river becomes first saturated with calcite and then with Mg-montmorillonite, magnesite, gypsum, thenardite, and at final step with sylvite. Consequently, the mechanism that controls the chemical evolution of groundwater in the study area is primarily related to evaporation processes.

On the other hand, the determination of ionic ratios (expressed in meq/L) of major ions in groundwater is a helpful tool for the identification and differentiation between groundwater bodies flowing through different water systems (Schoeller, 1956 and 1977; White et al., 1963; Kronfeld and Rosenthal, 1987; Rosenthal, 1987; Hem, 1992).

The Na/Cl ratio, which tends to increase in the Euphrates river from 1.4 to 1.7, is clearly higher than that of common waters in the hydrological cycle (0.86-1). This ratio suggests a further source of sodium, which could probably be due to seepage of saline water into the river. Also, the Na/Cl ratio of groundwater (0.8 to 1.88) was generally higher than 1, as a limit for common water in the hydrological cycle (Hem, 1992). This ratio implies a further source of sodium, which could be related to dissolution of thenardite (Na_2SO_4). This mineral was practically detected in a high quantity proportion (up to 40 %), together with halite (up to 65 %), in the mineralogical composition of the collected soil samples from the study area.

The Ca/SO_4 ratio ranges from 0.2 to 1.37, and thus the depletion of calcium versus sulphate is the consequence of the thermodynamic conditions controlling the equilibrium states between the groundwater and the carbonate minerals, suspected to be precipitated. The low SO_4/Cl ratio (0.6-1) in the groundwater, most affected by salinization (sites nos. 10-14), provides the evidence of high rate of halite dissolution with respect to gypsum.

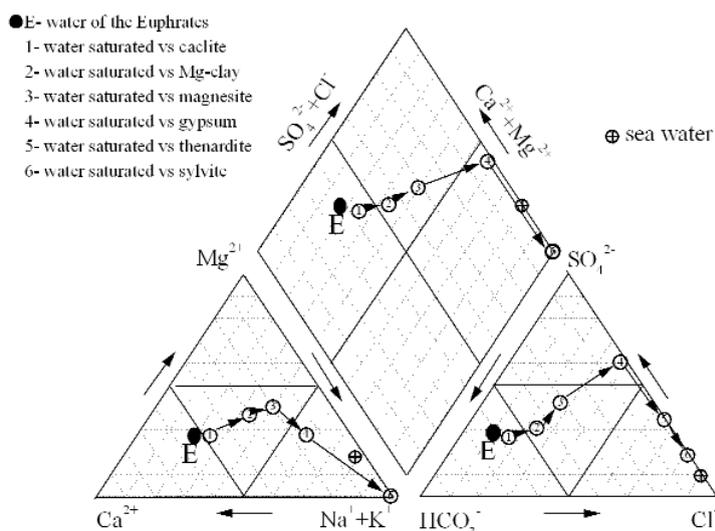


Figure 9. Evolution of the chemical composition of the Euphrates river water during evaporation in the Piper diagram (data from Dosso, 1980).

The thermodynamic equilibrium conditions controlling the water chemistry in the study area were also studied by applying the WATEQ4F and PHREEQE programs (Plummer et al., 1976; Appelo et al., 1992). The results show that all water samples, including those of the Euphrates river, were oversaturated with respect to both calcite and dolomite. A major part of groundwaters was also oversaturated with respect to magnesite, while those of the Euphrates were under-saturated or close to equilibrium with respect to this mineral. Although, most of the groundwater samples were under-saturated with respect to gypsum, few others (sites nos. 2, 11, 12, 13, 14 and 27) were found in equilibrium or slightly over-saturated with respect to this mineral.

Stable isotopes (^{18}O and ^2H) composition

The stable isotopes of ^{18}O and deuterium ^2H are widely used, as natural tracers, in isotope hydrological investigations (Fritz and Fontes, 1980; IAEA, 1980, 1981, 1983, 1987, 1991 and 1995; Verhagen et al., 1991; Kattan, 1995, 1997a and 1997b, 2001; Clark and Fritz, 1997). The use of these isotopes in water studies is based upon the concept that the process of isotopic fractionation between the different phases of water (ice, liquid and vapor) occurs as a result of different partial pressures of water molecules and diffusion velocities in air of the different isotopic species of water. (IAEA, 1981; Payne, 1983).

The results of the mean isotopic composition of water samples collected from the study area during the period 2000-2001; together with the deuterium excess values ($d = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}$) are reported in Table 1. These data permit the distinction between the following groups:

- 1) Groundwater of the sites nos. 26 and 27, which tends to have the most enriched stable isotope compositions ($-4.53\text{‰} < \delta^{18}\text{O} < -4.26\text{‰}$ and $-32.4\text{‰} < \delta^2\text{H} < -29.3\text{‰}$) as well as the lowest deuterium excess values ($3.9\text{‰} < d < 4.7\text{‰}$). The isotopic enrichment for this group is related to evaporation and low mixing processes with the Euphrates water.
- 2) The waters of the majority of the sampled sites, including those of the Euphrates and Khabour rivers, which show more depleted isotopic compositions ($-7.46\text{‰} < \delta^{18}\text{O} < -7.10\text{‰}$ and $-52.1\text{‰} < \delta^2\text{H} < -49.1\text{‰}$), together with higher deuterium excess values ($5.9\text{‰} < d < 9.7\text{‰}$), compared with those of the above mentioned group. This group reflects the relationship between the Euphrates river water and the surrounding groundwaters, mainly in terms of mixing.
- 3) Groundwaters of the sites nos. 5, 9, 11, 12, 14, 15 and 25, which show intermediate isotopic compositions between the above two mentioned water bodies. Although, groundwater of this group is less evaporated compared with those in the sites nos. 26 and 27, it can be observed that the sites nos. 5, 11 and 14 are characterized by the lowest deuterium excess values ($1.6 < d < 2.7$). This group of waters seems to be subjected to a rapid evaporation process compared with those in the sites nos. 9, 12, 15 and 25, which show also intermediate deuterium excess values ($4.7 < d < 8.2$).

The spatial distribution of the stable isotope values, together with the deuterium excess values in the study area (figures 10 and 11), clearly shows a gradual depletion of the stable isotope composition towards the Euphrates river course. These patterns coincide completely with the distribution patterns of E.C., TDS and major ion concentrations, indicating hence the effects of the mixing and evaporation processes.

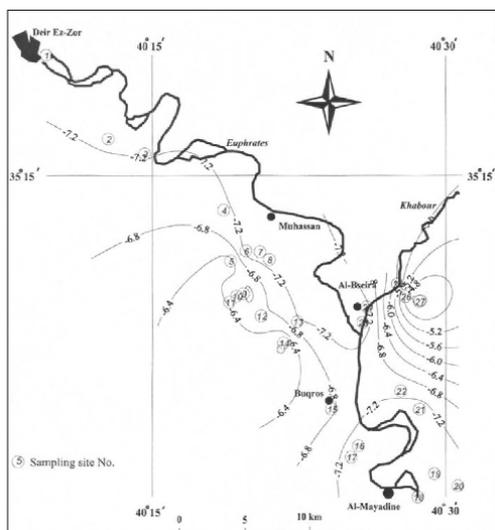


Figure 10. Spatial distribution of the $\delta^{18}\text{O}$ concentration (‰, SMOW) of the groundwater in the study area during 2000-2001.

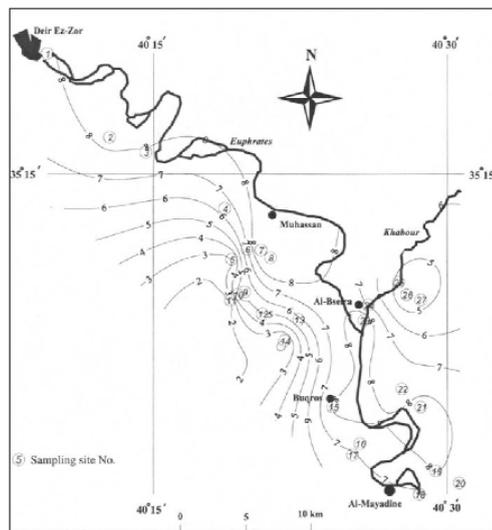


Figure 11. Spatial distribution of the deuterium excess value (‰, SMOW) of the groundwater in the study area during 2000-2001.

$\delta^{18}\text{O}$ - $\delta^2\text{H}$ relationship

Figure 12 illustrates the relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water samples collected in the study area, together with the plot of the isotopic composition of the Euphrates river water at the Syrian-Turkish border and at the exit of Al-Assad dam (Sajjad, 2000). All the water samples of the study area points, including those of the Euphrates, were more enriched with respect to those of the Euphrates at the Syrian-Turkish border, or at the exit of Al-Assad dam. Water sample points are generally distributed between two evaporation lines, with two different slopes (6.3 and 3.3), and each line starts from the point representing the isotopic composition of the Euphrates water at the Syrian-Turkish border. The reason for the slope divergence from the value (8) is because that evaporation does not take place under equilibrium condition (Craig, 1961). In fact, waters having undergone appreciable evaporation would usually have a slope in the range 4-6 (Gat, 1981; Payne, 1983).

The difference observed in the slope values could indicate a different mechanism of evaporation. This mechanism is mainly related to the water table depth from the bare soil, as well as to the distance from the river course. This means that the slope of 6.3 is due to low or absent of direct evaporation from a rather deep groundwater table below the land surface, as it seems for the sites nos. 26 and 27. Whereas, the slope of 3.3 value reflects, most probably, a direct evaporation of groundwater from a shallow water table. This later case could be accelerated by the lost of water through the phenomenon of capillarity movement. Consequently, it seems that the rapid and direct evaporation from the water table is rather important in the sites nos. 5, 11, 12 and 14, where the groundwater table was of less than 2 m below the earth's surface.

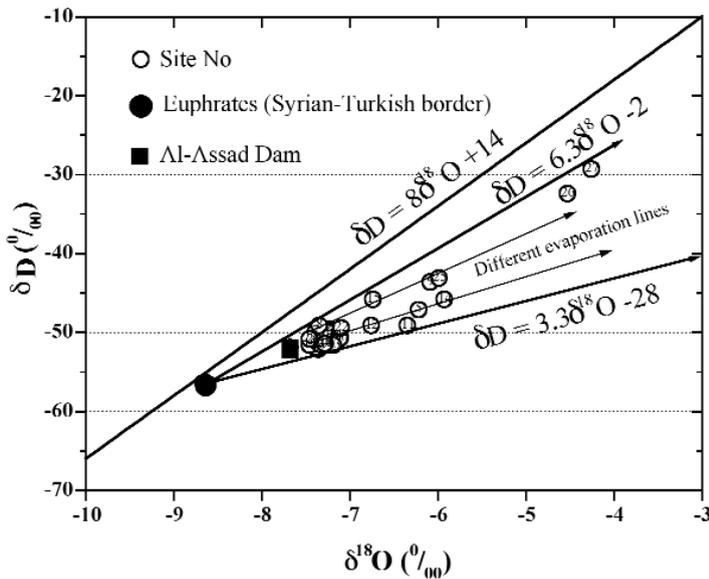


Figure 12. Relationship between $\delta^{18}\text{O}$ and δD values of water samples collected from the study area during 2000-2001.

Stable isotopes and groundwater salinization

Stable isotopes can be successfully used to assess the origin of salinity and identify the mechanisms of groundwater salinization (IAEA, 1981 and 1983). As groundwater percolate in a unique water system, the stable isotope composition of groundwater is usually constant and is not subject to any change, whereas, the chemical composition of groundwater in the same system would ordinary increase in function of the water movement, and may also change its type (Schoeller, 1977; Hem, 1992). Hence, the isotopic approach, which is usually considered, is based on the concept that salinization originated from the dissolution of salts is not accompanied by any significant changes in the stable isotopic composition of the leaching groundwater, and thus the salinity remains independent of the isotopic composition (IAEA, 1983).

Contrarily, the isotopic composition of water under mixing and/or evaporation processes is necessarily accompanied by sensitive changes in its stable isotopic composition, which could be related to the fraction of the admixed end-members or the degree of evaporation factor. Consequently, when salinity increases as a result of evaporation, a positive relationship would exist between the stable isotopic composition and the conservative ionic species. Obviously, when salinity is derived from the dissolution and flushing salts, the resulting isotopic composition will not show any change in function to the increasing salinity (IAEA, 1983).

The relationships between $\delta^{18}\text{O}$ compositions and SO_4^{2-} , and between $\delta^{18}\text{O}$ and TDS values, are illustrated in figures 13 and 14. These plots suggest the existence of two processes for the increasing salinity in the study area:

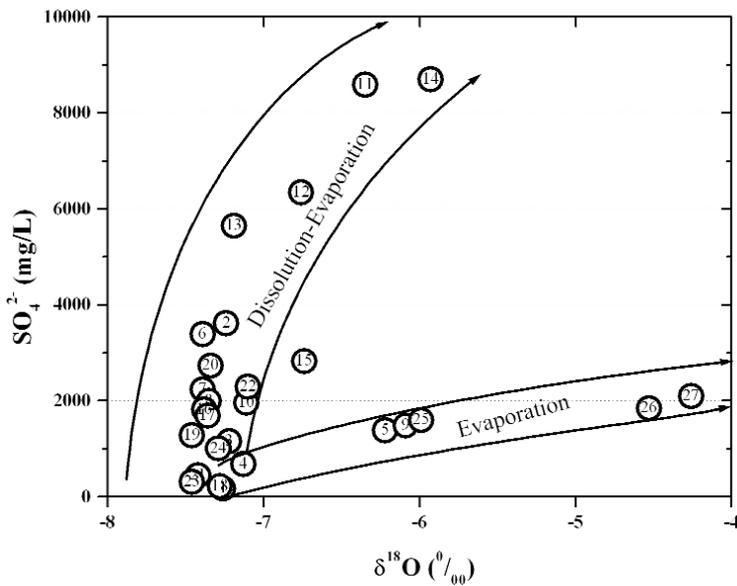


Figure 13. Relationship between $\delta^{18}\text{O}$ and SO_4^{2-} concentration of the water in the study area.

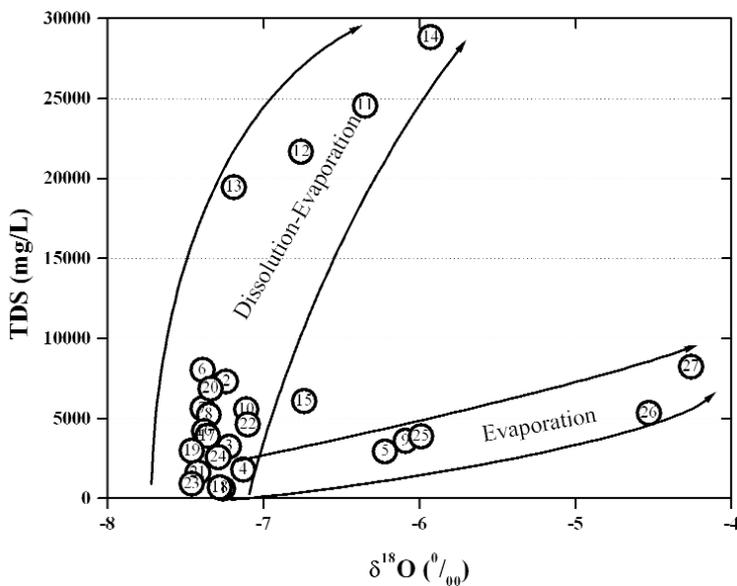


Figure 14. Relationship between $\delta^{18}\text{O}$ and TDS contents of the water in the study area.

- 1) Enrichment by evaporation only. This process generally affects groundwaters in sites nos. 5, 9, 25, 26 and 27, for which a rather linear correlation exists between the chemical parameters and the $\delta^{18}\text{O}$ composition.
- 2) Enrichment by both evaporation and salt dissolution. These two processes tend simultaneously to affect, mainly sites nos. 11-14, where the TDS content was of more than 15 g/L. The origin of the salinity in the remaining other sites, could also be due to these two processes. But, as these sites are more or less close to the Euphrates river course, their salinity contents reflect the mixing processes with the Euphrates river water. Also, as it can be seen in Table 1, the low value of tritium content (4-5 TU) in sites nos. 14, 26 and 27, proves that the mixing with the Euphrates river water in these sites is limited, since the tritium content in this river was of about 9-11 TU.

General conclusions

The combination of both hydrochemical and isotopic investigations of surface and groundwater in the down-stream valleys of the Euphrates and Khabour rivers has aided to better characterize the main features of salinization of local groundwaters and soils in this sector. The general conclusions, that can be learned from this study, are the following:

- The Euphrates river water is rather fresh ($450 < \text{TDS} < 750 \text{ mg/L}$), and its TDS content had slightly increased within the last two decades, most probably as a result of seepage of saline water in the Euphrates river. The chemistry of the Euphrates river water was of a calcium-sodium and sulphate-bicarbonate and -chloride type, and it differs largely from that of local groundwaters, which were more saline and tend to evolve towards a sodium- chloride and -sulphate type.
- Groundwaters in the study area were primarily originated from the Euphrates river water, either by lateral direct inflow from the river or by a vertical percolation of the irrigation water (entirely from the Euphrates river) towards the water table.
- The chemistry of groundwaters reflects the importance of the evaporation processes in this dry region, and it completely agrees with the thermodynamic simulation of the evaporation of Euphrates river water.
- The spatial distribution of major ions, stable isotopes and tritium concentrations leads to detect a gradual mixing between local groundwater and the Euphrates river water. The contribution of the river component becomes larger with the decreasing distance from its course.
- The salinization of groundwater is due to three major species: sodium, chloride and sulphate, mainly derived from the dissolution of halite (NaCl) and thenardite (Na_2SO_4). These minerals were largely detected on the soil surface, as a result of irrigation under high potential evaporation.
- The maximum groundwater salinity, which was clearly observed in the sites nos. 10-14, could be the consequence of three main factors: 1) groundwater movement towards this zone, which could enhance dissolution of further amounts of salt rocks; 2) the localization of this zone rather far from the Euphrates river course, and thus mixing and dilution processes were low; and 3) the localization of this zone close to a gypsum-rich substratum.
- The stable isotope composition of waters permits the distinction between three groups: 1) the isotopically enriched groundwater by evaporation process from rather deep water table and from sites relatively far enough from the Euphrates river course (sites nos. 26 and 27); 2) the Euphrates river water and the majority of groundwaters, rather close to the river course, which were less

affected by evaporation processes; and 3) groundwater of intermediate position between the above two mentioned groups (sites nos. 5, 9, 11, 12, 14, 15 and 25), which seems to be formed as a result of low mixing process with the river water, but under direct evaporation from the shallow ground water table.

- The relationships between stable isotopes and major ions suggest the existence of two processes for the increasing salinity: 1) enrichment as a result of evaporation only, such as the salinity in the sites nos. 5, 9, 25, 26 and 27; and 2) enrichment by both evaporation and dissolution of salt minerals. The later case corresponds practically to the sites nos. 11-14, which belongs to the most affected salinization zone. The low salinity in the remaining sites reflects the intensity of the mixing process with the Euphrates river water.
- The presence of high tritium content in groundwater confirms that groundwater resources in this zone are of recent age and annually renewable.
- The absence of a real and a practical drainage system, together with a high evaporation rate and a shallow water table, are directly or indirectly the primary reasons for the continuous soil salinization and the increasing salinity of groundwaters in the study area.

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