

Research Article

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Determination of Recharge by Means of Isotopes and Water Chemistry in Shaqlawa-Harrir Basin, Kurdistan Region, Iraq

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Abstract

Stable isotopes (²H, ¹⁸O), ¹⁴C determination, and chemical analysis of deep groundwater and surface waters (river and springs) were used to investigate the sources of ground- and surface water, groundwater recharge mechanisms as well as possible sources of ions in groundwater in the semi-arid Shaqlawa-Harrir basin in Kurdistan. One hundred water samples were taken during wet and dry season. The d-excess varies significantly depending on temperature and humidity at the vapor sources. The means of the δ 18O and δ 2H values in the groundwater samples are -6.8 and -36.8‰, for the spring samples -6.3 and -34.5‰, and for the river samples -9.2 and -51.3‰, respectively. The depletion in the δ ¹⁸O content of some water samples is due to the higher altitude of some recharge areas (altitude effect). ¹⁴C data ranges from 3.4, 71.4 and 82.7 pmC and shows that recharges rates and means residence times vary greatly in the study area. Groundwater was mainly classified as Ca-Mg-HCO₃ and Mg-Ca-HCO₃ type; only five well water samples belong to the Na-Ca-HCO₃ type. All water samples investigated are suitable to be used as both drinking water and irrigation water.

Keyword: Stable isotope; Recharge source; Radio-active isotope; Groundwater age; Hydrochemistry; Semi-arid area

Introduction

Stable isotopes in groundwater hydrology give a direct insight into the movement and distribution processes within the aquifer. Environmental isotope techniques in hydrogeological investigations are very helpful for studying, utilizing, managing and developing water resources [1,2]. These techniques are suitable for solving water resource problems, especially in semi-arid areas where water resources are rare and the importance of groundwater increases. Environmental isotopes provide additional information about the origin of the water, storage properties, water dynamics (relations between surface and groundwater), and groundwater contamination [3-5].

Stable isotopes can be useful for distinguishing the sources of surface water and groundwater discharges. Depending on the altitude where the recharge occurs, groundwater may have special isotopic signatures [5]. Some regional environmental isotope studies were undertaken in the study area related to hydrogeological and hydrological conditions; Mawlood determined a Local Meteoric Water Line (LMWL) for Haji Omaran-Erbil city according to the data of two meteorological stations located in Syria (Halab) and in Turkey (Adana) [6]. Also, Al Manmi investigated the stable isotopic composition of major aquifers in the Rania area, Sulaymania city, to distinguish the sources of the groundwater and to determine the relation between altitude and $\delta^{18}O$ [7]. Hamamin and Ali determined an LMWL by continuous monitoring and taking regular monthly samples, they established a $\delta^{18}O$ -altitude relationship based on groundwater and surface water samples taken in the Basara basin, Sulaymania, Kurdistan [8].

In Kurdistan region of Iraq demand for freshwater has risen dramatically because of the growth of the population and the establishment of agricultural and industrial projects. Therefore, groundwater utilization has become more important for the Shaqlawa-Harrir area. The main objectives of this work were to investigate the ground and surface water sources, the groundwater recharge mechanism, the possible sources of ions in the groundwater, and to understand the hydrogeological processes and the hydrochemical characteristics of the groundwater from the different aquifers and surface water to discuss the possibility of using groundwater for drinking (human and animal consumption), agricultural and industrial purposes. This study aims as well to determine the groundwater age, flow paths, and to quantify the mixing of groundwater between aquifers by using stable isotopes (δ^{18} O and δ^{2} H) and radiocarbon (¹⁴C).

Materials and Methods

Study area description

The Shaqlawa-Harrir basin is located in the northeast of Erbil city, extending between 44° 2' – 44° 34' E and 36° 11' – 36° 39' N. The area covers about 1150 km² with elevations ranging from 350 to 1500 m above sea level within the high folded zone [9,10]. The area is bounded by the Greater Zab River in the northwest, the Harrir anticline in the northeast and the Safin anticline in the southwest. The Shaqlawa-Harrir basin is divided into two major basins, Shaqlawa and Harrir basin, and three small basins: Tawska, Hiran and Harash (Figure 1).

The climate in the basin belongs to the semi-arid Mediterranean type. It is characterized by cold, rainy winters on the one hand and long, hot, dry summers on the other hand. Meteorological data obtained from the ground meteorological station in Salahaddin district/Erbil Governorate (Pirmam meteorological station) for the period between 1992 and 2012 show that the annual precipitation is about 589 mm, with maximum and minimum mean monthly relative humidity of 71.7% in January and 33.9% in July, respectively. The maximum monthly temperature is about 35.5°C in July and the minimum is about 8.1°C in January (Figure 2).

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Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Rainfall (mm)	113.3	111.1	90.6	64.2	24.8	1.5	0.8	0.02	3.7	35.7	55.1	88.6
R.H* %	71.7	70.9	59.6	57.7	43.9	34.3	33.9	34.9	38.6	49.1	59.1	64.4
Temperature (°C)	8.1	9.1	13.5	18.9	25.4	31.13	35.5	35.5	30.8	24.7	15.3	10.3
Sunshine (h/d)	4.6	4.9	6.2	6.6	8.98	11.5	11.7	10.7	9.9	7.6	6.2	5.1
Wind Speed (m/s)	2.0	2.4	2.8	2.9	2.6	2.7	2.4	2.3	2.1	2.2	1.9	1.9
Evaporation (mm)	32.5	38.4	94.2	116.1	188.9	253.9	266.7	258.8	180.7	122.7	53.4	43.0

* Relative Humidity

Table 1: Mean monthly climatic parameter of Shaqlawa-Harrir basin for the period 1992-2012, Pirmam meteorological station.



The maximum mean monthly evaporation is 266.7 mm in July and the minimum is 32.5 mm in January. The mean annual sunshine duration is 7.8 h/d, and the wind speed in the study area ranges from 1.9 to 2.9 m/s; the annual mean wind speed is 2.4 m/s (Table 1).

Geological and stratigraphic framework

The exposed geological units are represented by 11 formations which date from Early Cretaceous to Pliocene and Quaternary deposits, represented by alluvial deposits of Holocene age and river terraces of Pleistocene age. The oldest unit of Lower Cretaceous age is the Qamchuqa formation which is predominantly carbonate and forms the core of most of the anticlines in the area. The Upper Cretaceous formations are represented by carbonate rocks of the Bekhme formation and impure carbonate rocks of the Shiranish formation. The sequence is followed by alternating flysch and carbonate sediments of the Kolosh, Khurmala, Gercus and PilaSpi formations (Table 2 and Figure 3). The geological cross section is shown in Figure 4.

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Age	Geological Units	Lithological Composition
Holocene	Recent alluvial deposits	Different sized clastics, mixture of clay, sand & pebbles.
Pleistocene	River Terraces	Mixture of clay, sand & pebble.
Pliocene	Bai Hassan & Muqdadiya Formation	Thick sandstone, siltstone & conglomerate.
Late Miocene	Injana Formation	Massive beds of claystone & sandstone.
Middle Miocene	Fatha Formation	Alternation of sandstone, claystone, limestone & rare evaporation.
Middle-Late Eocene	PilaSpi Formation	Dolomitic limestone overlain by recrystallized & chalky limestone
Early Eocene	Gercus Formation.	Red mudstone, sandstone & shale, with rare conglomerate.
Paleocene	Kolosh Formation	Mainly clastics: shale, limestone, marl & mudstone.
Late Cretaceous	Shiranish & Tanjero Formations	Blue marl overlaying limestone & marly limestone.
Middle Cretaceous	Aqra-Bekhme & Qamchuqa Formations	Bituminous dolomitic limestone; massive organic limestone.

Table 2: Age and lithological description of the geological units.



Relatively impermeable rocks represented by the Kolosh, Gercus, Fatha and Injana formations and in some cases fine alluvium sediments, which cover the central and northwestern parts of the basin, have a great impact on impeding the infiltration of water to the groundwater within the basin. The development of the basin is attributed to the structural, stratigraphic and geomorphological setting of the area. The formation of numerous large anticlines and synclines with a NW–SE axis parallel to the main structural setting are good examples of intensive uplifting and folding of geological formations during the Alpine Orogenic phases. This uplift process has significantly influenced the recharge and discharge rates to and from the basin [11].

Aquifer system

Three types of aquifers exist in the Shaqlawa-Harrir basin: karstic, fissured-karstic and porous aquifers. Karst aquifers are represented by the Bekhme formation which forms an inhomogeneous anisotropic

aquifer containing large groundwater reserves. This aquifer is characterized by its very high permeability and transmissivity and by its turbulent water-flow regime. Wells in it have high specific yields and the drawdown values are very small. Most freshwater in the Shaqlawa-Harrir basin is produced from this aquifer.

Fissured-karstic aquifers are represented by the PilaSpi, Kolosh and Gercus formations containing medium to large groundwater reserves. These aquifers are characterized by high permeability and transmissivity, but to a lesser extent than those in the karstic aquifer mentioned before [12]. They are developed in limestone, dolomites, marly limestones, and dolomitic limestones and are most important for the irrigation and water supply of large areas. The flow regime in the PilaSpi formation is turbulent.

Porous aquifers are represented by the Bai Hassan and Muqdadeya formations, including overlying Pleistocene terraces and recent





alluvium deposits. Typical characteristics of these aquifers are the inter-bedded layers of fine, medium, and coarse-grained textures and variations in permeability from one site to another within the same aquifer horizon.

The Injana, Fatha, and Kolosh formations contain groundwater in limited and varying quantities. Impermeable layers like claystones or marls partly alternate with permeable rocks, such as fractured limestone, resulting in low permeability and limited groundwater presence. This rock complex represents either aquitards or even a fully impermeable barrier to groundwater flow (aquiclude).

There are four types of deposits in the study area, Pliocene deposits (the Bai Hassan and Muqdadeya formations), Middle and Upper Miocene deposits (Injana and Fatha formations), Paleocene and Eocene deposits (PilaSpi, Kolosh, and Gercus formations) and Cretaceous deposits (Aqra-Bekhme, Qamchuqa and Shiranish formations) (Figure 5).

Water sampling and analysis

One hundred water samples were collected during the wet season (spring 2012) and the dry season (fall 2012) to investigate seasonal variations. A total of forty groundwater samples (4 deep well samples from confined aquifers and 36 from unconfined aquifers), nine spring samples and one river sample were taken. pH, eH, T, EC, O_2 were read until constant values were achieved before the samples were collected. Samples for cations and anions were filtered through cellulose acetate filters (0.2 μ m) into 50 ml polyethylene bottles. Samples for total inorganic carbon and dissolved organic carbon were collected in 100 ml glass bottles; samples for stable isotopes were collected in 30 ml polyethylene bottles and filtered in the laboratory; and three samples were collected for ¹⁴C in 1 L polyethylene bottles.

Analysis of the stable isotopic composition (δ^2 H and δ^{18} O) was undertaken using a Liquid-Water Isotope Analyzer (LWIA, model 908-0008-3001) of Los Gatos Research (LGR). Using the high performance mode, precision for δ^2 H and δ^{18} O was ± 1 ‰ and ± 2 ‰, respectively. The values are reported according to V-SMOV.

Rainwater samples could not be taken during the study. Therefore,

we refer to the LMWL of Hamamin and Ali [8], which was obtained from sampled rainwater of 55 events during the period from December 2009 to June 2010 at the Bazian meteorological station (about 140 km to the northwest of the Shaqlawa-Harrir basin):

$$\delta^2 H = 7.7 \, \delta^{18} O + 14.4$$
 (1)

Also, we refer to the Mediterranean meteoric water line of McGarry et al. [13]:

$$\delta^{2}H = 8\delta^{18}O + 22$$
 (2)

¹⁴C was determined by converting the dissolved inorganic carbon to CO_2 by adding concentrated phosphoric acid to a 1L water sample which was constantly stirred. The released gas was sampled in an evacuated quartz ampoule. The CO_2 gas ampoules were sent to the Poznań Radiocarbon Laboratory, Poland, to determine the percentage of modern carbon (pmC) using an accelerator mass spectrometer (1.5 SDH-Pelletron Model "Compact Carbon AMS" of the National Electrostatics Corporation, Middleton, USA).

Major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺ and Li⁺) and anions (SO₄²⁻, Cl⁺, F⁻ and NO₃⁻) were determined with ion chromatography (Metrohm-Compact IC Pro). Trace elements (B, Ba, Zn, Sr, Al, Sc, Cr, P, Cr, Mn, Fe, Co, Cu, Zn, As, Se, Br, Rb, Mo, Ag, Cd, Sn, Sb, Cs, La, Ce, Eu, Pb, Si, and U) were analyzed with ICP-MS (Thermo Scientific-XSERIES 2). Total Inorganic Carbon (TIC) and Dissolved Organic Carbon (DOC) were measured with an Elementar LiquiTOC.

The percentage of sodium, Sodium Adsorption Ratio (SAR), Residual Sodium Carbonate (RSC), and soluble sodium percentage possible (SSPP) were calculated according to:

$$SAR = \frac{Na^{+}}{\sqrt{\frac{1}{2}(Ca^{2+} + Mg^{2+})}} \text{ in } meq/L$$
(3)

$$Na\% = \frac{Na^{+} + K^{+}}{Ca^{2^{+}} + Mg^{2^{+}} + Na^{+} + K^{+}} *100$$
(4)

$$SSPP = \frac{Na^{+}}{(Ca^{2+} + Mg^{2+} + Na^{+}) - (Co_{3}^{2-} + HCo_{3}^{-})} *100$$
(5)



$$RSC = (Co_{1}^{2-} + HCO_{1}^{-}) - (Ca^{2+} + Mg^{2+})$$
 in meq/L (6)

PHREEQC was used to check the charge balance, compute the aqueous speciation and the saturation indices of certain minerals by using the database wateq4f.dat [14]. The ionic charge balance was less than \pm 5%.

Interpolation and statistics

Spatial interpolation by means of Kriging was used to plot the distribution of isotopes and major ions (Figures 7,10,12 and 13). Kriging assumes that the distance or direction between sample points reflects a spatial correlation which used to explain variation in the surface. This method is a powerful geostatistical interpolation technique based on the spatial correlation of sampled points [15]. The Kriging tool fits a mathematical function to a specified number of points to determine the output value for each location. Kriging is most appropriate when you know there is a spatially correlated distance or directional bias in the data. The interpolation was performed by means of ArcGIS version 10.1. Statistical analysis (e.g. Kruskal-Wallis test) was done by SPSS version 16.

Results and Discussion

Isotopic composition of surface and groundwater

In semi-arid regions water might have rather long residence times in the top few meters of soil. The kinetic effect of water vapor diffusion from the unsaturated zone might have a greater impact on the isotopic composition of the water than fractionation due to evaporation from surface water might have [16,17]. Therefore, evaporation from the unsaturated zone is predominantly characterized by stronger evaporative enrichment with a lower slope of the isotopic composition.

The mean of the δ^{18} O and δ^{2} H values for the wet season in the groundwater samples were -6.6 and -36.5‰, in the spring samples -6.3 and -34.3‰, and in the river water -9.4 and -52.4‰, respectively. During dry season, δ^{18} O and δ^{2} H in groundwater were -6.9 and -37.2‰, in the springs -6.3 and -34.7‰, and in the river water -8.7 and -50.1‰, respectively (Table 3).

All samples plot above the GMWL, which reflects the significant impact of precipitation of water vapor originating from the closed basins. The regression lines of the samples have different slopes, which either means evaporation effect or water-rock interaction [18] (Figure 6). The d-excess of the LMWL (14.4) is larger than the d-excess of the GMWL (10). This can be explained as the effect of mixing with vapor originating from the Mediterranean Sea cyclone, which is characterized by higher deuterium excess values due to the elevated relative humidity of the atmosphere. Some groundwater samples plotting above the LMWL indicate recharge from local rain events and high elevation areas with different wind speeds and temperatures. Spring samples and some groundwater samples plot on or near the LMWL, because of the altitude effect. Few groundwater samples plot below the LMWL and close to the GMWL which indicates another source of precipitation in the area originating from the Persian Gulf. The river samples plot above the LMWL because the source of the river originates from the Taurus Mountains, Turkey. The lower d-excess for the LMWL than the MMWL indicates a less evident evaporation effect in the study area. Indeed, the d-excess varies significantly depending on the temperature and humidity of the vapor's source region.

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The isotopic composition is depleted in the groundwater from karstic and fissured-karstic aquifers, while it is enriched in the porous aquifer. These isotopically heavier groundwater samples from the porous aquifer as compared to the karstic and fissured-karstic aquifers may be attributed to the impact of evaporation before or during infiltration. The porous aquifer receives most of the recharge from precipitation. During

	Sample Type A	Aquifer Type	Location (UTM)		Elevation		Wet Season		Dry Season			
SN	Sample Type	Aquiter Type	Easting	Northing	(m) a.s.l	δ²H ± 2	δ ¹⁸ O ± 1	d excess	$\delta^2 H \pm 2$	δ ¹⁸ O ± 1	d excess	
1	D.W	F.K	434565	4029794	855	-38.4	-6.7	15.0	-38.2	-7.4	20.6	
2	D.W	F.K	436826	4026925	982	-39.4	-7.2	17.9	-39.6	-7.6	21.3	
3	D.W	F.K	439260	4024480	1190	-39.4	-7.5	20.9	-39.2	-7.5	20.5	
4	D.W	F.K	442401	4021134	1190	-39.4	-7.5	20.6	-39.5	-7.5	20.5	
5	D.W	F.K	445706	4018649	1139	-40.2	-7.5	19.7	-39.7	-7.4	19.5	
6	D.W	F.K	449501	4014632	1041	-38.7	-7.3	19.6	-38.3	-7.1	18.6	
7	D.W	F.K	447231	4017831	1088	-40.1	-7.6	20.4	-39.7	-7.5	19.9	
8	D.W	F.K	450540	4018701	1011	-40.3	-7.7	21.4	-39.5	-7.5	20.4	
9	S	к	454550	4014850	925	-40.4	-7.8	21.9	-40.0	-7.5	20.1	
10	D.W	F.K	454249	4015254	962	-39.7	-7.7	22.0	-40.0	-7.6	20.4	
11	D.W	F.K	454109	4015105	978	-39.2	-7.6	21.9	-39.8	-7.5	20.2	
12	D.W	F.K	446219	4021918	1044	-39.0	-7.4	19.9	-38.8	-7.3	19.9	
13	D.W	к	445194	4025489	959	-35.0	-6.7	18.5	-35.5	-6.7	18.0	
14	D.W	F.K	437470	4029479	1015	-38.1	-7.2	19.7	-38.6	-7.3	19.4	
15	D.W	F.K	441109	4027518	987	-40.7	-7.6	20.2	-41.8	-7.9	21.5	
16	D.W	P	442463	4032525	871	-33.0	-6.1	15.4	-32.5	-6.0	15.4	
17	D.W	ĸ	445724	4034192	805	-37.2	-6.8	17.3	-36.9	-6.9	18.5	
18	D.W	E.K	445563	4035420	777	-39.0	-7.1	18.2	-38.8	-7.3	19.3	
19	S	FK	445441	4036667	744	-38.4	-7.0	17.2	-38.5	-7.2	19.3	
20	S	ĸ	447906	4038217	861	-39.7	-7.3	18.7	-39.5	-7.6	21.3	
21	DW	ĸ	444936	4041578	762	-35.1	-6.1	13.7	-38.9	-6.9	16.5	
22	D.W	FK	443686	4043931	774	-39.4	-7.2	18.1	-39.5	-7 1	17.0	
22	D.W	EK EK	440000	4040301	781	-30.7	-7.3	18.6	-30.0	-7.2	17.8	
23	D.W	FK	438756	4051244	616	-30.7	-7.3	18.7	-33.3	-7.3	18.6	
25	D.W	FK	436619	4053091	633	-37.8	-7.0	18.0	-38.5	-7.1	18.1	
26	S	FK	435472	4053369	634	-33.8	-6.4	17.3	-34.1	-6.5	17.6	
20	S	EK EK	132855	4054601	556	-20.7	-53	13.0	-30.8	-5.7	14.6	
21		D	432033	4053458	/83	-20.7	-5.3	12.0	-20.7	-5.7	15.5	
20	D.W	ĸ	426356	4053458	382	_31.0	-5.5	12.0	-38.0	-6.9	16.5	
30	D.W	EK	423239	4051304	379	_41 7	-6.9	13.6	-38.5	-7.1	18.5	
31	P	1.10	423263	4051506	368	-52.4	-9.4	22.8	-50.0	-8.7	10.0	
32	S	D	425821	4052478	407	-32.4	-5.5	15.3	-28.7	-5.5	15.5	
33		D	426842	4032470	370	-20.4	-5.8	13.3	-20.7	-6.0	13.0	
34	D.W	ĸ	4/3621	4038528	7/1	-31.4	-5.7	14.4	-33.0	-6.0	14.3	
35	D.W	EK	/37716	4052001	606	_30.1	-7.2	18.1	-30.4	-7.2	17.0	
36	S.W	P	430969	4050700	196	-30.0	-7.2	12.0	-30.8	-5.4	12.6	
37		P	425603	4030733	648	-32.0	-5.8	14.6	-33.1	-6.0	14.6	
38	S.W	ĸ	426026	4043286	627	-32.0	-3.0	17.3	-33.1	-0.0	16.21	
30		ĸ	420020	4046402	510	34.4	65	17.3	3/ 1	6.1	14.6	
40	0.00	P	429110	4040402	503	-34.4	-0.5	16.8	-34.1	-0.1	14.0	
40		P	428404	4049399	446	32.6	-5.9	13.0	32.4	-5.0	14.0	
42	D.W	P	430723	4046385	522	-31.3	-5.7	14.2	-32.4	-5.0	14.0	
12	D.W	r. K	433337	4044494	522	32.0	-5.1	0.0	3/6	-5.7	13.0	
43		ĸ	400007	4044404	653	-30.6	-5.4	9.9 10.2	-34.0	-0.1	10.0	
44	D.W	IX K	432639	4042191	707	-33.0	-5.4	12.3	-34.4	-0.4	15.4	
40	D.W	ĸ	435647	4037431	754	-33.0	-0.7	12.4	-34.1	-0.2	15.4	
40	D.W	ĸ	400047	4033138	070	-33.3	-5.0	12.4	-55.2	-0.4	15.0	
4/	D.W	r. V	400010	4033622	0/0 100F	-34.7	-0.0	13.4	-33.2	-0.4	10.7	
40	D.W	ĸ	400000	4019720	072	-30.2	-0.7	1/.0	-30.0	-1.4	20.4	
49 50	0.00	EK.	450066	4023133	074	-35.6	-0.0	16.0	-36.7	-7.0	13.0	
- 50	1 3	1.1	+00900	40231/3	5/4	-55.0	-0.4	10.0	-55.7	-0.1	13.4	

SN: sample number, D.W: deep well sample, S: spring sample, F.K: fissured-karstic aquifer, K: karstic aquifer, P: porous aquifer. **Table 3:** Isotopic data for Shaqlawa-Harrir area during wet and dry season in ‰.

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Figure 6: Relation between 6'H and 6'®O for 100 samples during two periods; A-deep well samples taken during wet season, B-deep well samples taken during dry season, C-spring and river samples taken during wet season, and D-spring and river samples taken during dry season, plus GMWL [18] MMWL [13] and LMWL [8].

rainfall within the plain area, rainwater accumulates and is exposed to evaporation resulting in an enrichment of heavier isotopes and then infiltration into the porous aquifer. The karstic and fissured-karstic aquifers receive the recharge from the surrounding highly elevated area. The high altitude contributes to more depletion in heavy isotopes in rainwater, and the joints and fractures of these aquifers supply good paths for transporting this infiltrated rainwater to the lower area. Stable isotope data can be used to estimate the flow of groundwater from adjacent aquifers because of the hydraulic interconnection between aquifers with contrasting compositions.

The difference in isotopic composition supports the existence of different recharge sources in the area and the altitude effect. The distribution of the isotopic composition shows that in the mountain areas heavy isotopes are more depleted than in the plain area (Figure 7).

Altitude effect

The mean altitude effect of the different aquifers was determined by assessing the δ^{18} O content of the water samples and the altitude. The mean δ^{18} O of the karstic aquifer samples is -6.2‰, that of the fissuredkarstic aquifer samples is -7.3‰, of the porous samples is -5.79‰, and that of the carbonate spring samples is -6.61‰. The result of the regression line was estimated and shows that the δ^{18} O content of the water samples decreases with the increase in altitude (Figure 8).

By using the non-parametric Kruskal Wallis test it was shown that the differences between the aquifers are significant on a significance level of \leq 0.001 (Figure 9). Interpolation of the ¹⁸O data of the basin shows that the effect of high elevation of the recharge is clearly represented by more negative isotopic signature along the southwestern border with the Safin and Pirmam Mountains, and Harrir Mountain in the eastern part of the basin as compared to the less negative values in the northern parts toward the Greater Zab River.

Radiocarbon (14C)

 $^{14}\mathrm{C}$ was analyzed in two water samples, well sample (S-49) and spring sample (S-38) in the karstic aquifer. A third $^{14}\mathrm{C}$ value (well sample S-23) in the fissured-karstic aquifer was provided by (Ahmed M, Salahaddin University, Kurdistan region, personal communication, 2013). The differences in $\delta^{13}\mathrm{C}$ between soil-derived TIC and carbonate minerals in the aquifer can provide a reliable measure of $^{14}\mathrm{C}$ dilution by carbonate dissolution. The $\delta^{13}\mathrm{C}$ mixing model allows for incorporation of $^{14}\mathrm{C}$ -active TIC during carbon dissolution under open system conditions, and subsequent $^{14}\mathrm{C}$ dilution under closed system conditions (Table 4).

The q-factor according to Pearson [19] and Pearson and Hanshaw [20] was obtained from carbon isotope mass balance as:

$$q = \frac{\delta^{13}C_{TIC} - \delta^{13}C_{carb}}{\delta^{13}C_{Soll} - \delta^{13}C_{carb}}$$
(7)

where $\delta^{13}C_{_{TIC}}$ = measured ^{13}C in groundwater, $\delta^{13}C$ soil= $\delta^{13}C$ of the soil CO₂ (usually close to -23‰), and $\delta^{13}C_{_{carb}}$ = $\delta^{13}C$ of the calcite being dissolved (usually close to 0‰).





Figure 7: Distribution of the isotopic composition (δ²H and δ¹⁸O) in Shaqlawa-Harrir Basin for different aquifers; (A & B): fissured karstic aquifer; (C & D): karstic aquifer; (E & F): porous aquifer.









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The ¹⁴C activity of well S-23 in the unconfined aquifer (fissuredkarstic) with a corrected ¹⁴C age of 1667 \pm 43 y BP and the artesian well S-49 in the confined karstic aquifer with a corrected ¹⁴C age of 970 \pm 35 y BP indicate either a rather low flow velocity or has to be interpreted as biased by additional chemical reactions. This is likely and proof once more that ¹⁴C is anything but an ideal tracer to determine mean residence times in limestone aquifers.

Samples	S-23	S-49	S-38			
¹⁴ C pmC	71.4	71.4 82.66				
¹⁴ C age (uncorrected) BP	2416 ± 43	1529 ± 35	27233 ± 410			
δ ¹³ C _{τις}	-16.05	-14.6	-21.1			
δ ¹³ C _{soil} (‰)	-23	-23	-23			
δ ¹³ C _{carb} (‰)	0	0	0			
q	0.69	0.63	0.91			
¹⁴ C age (corrected) BP	1667 ± 43	970 ± 35	24782 ± 410			

Table 4: The parameters of the ¹³C mixing model for ¹⁴C age correction.

The very low ¹⁴C activity of S-38 (carbonate spring) in the karstic aquifer with a corrected ¹⁴C age of 24782 ± 410 y BP would indicate an extreme long residence time of groundwater in the fractures of the bedrock. But this is contradiction with the data from stable isotopes, which do not show any evidence for recharge during cold climate (fossil water recharged during the last ice age). Reasons for the low ¹⁴C value are either admixture of volcanic CO, or oxidation of organic matter contained in the aquifer. Volcanic $\rm CO_2$ contains no $^{14}\rm C$ and will dissolve carbonate with no 14C and thus significantly bias the 14C pattern. In case of oxidation of organic matter the ¹⁴C signal of the organic matter is one further unknown variable depending on the age of the organic matter. Depending on the oxidation process (O₂, NO₂, SO₄ CH₄) and the origin of the organic matter a δ^{13} C correction is often not applicable in such cases [21,22]. Because volcanic CO₂ is rather unlikely in the given geologic setting it is assumed that organic matter is the reason for the very low ¹⁴C values. Light δ^{13} C values from CH₄ oxidation can be compensated by heavy δ^{13} C values of limestone leading to the 21.1‰ determined in sample S-38.

	Linit	Lipit		rstic aquifer			Karstic	aquifer			Porous	aquifer	
Par⁺	Unit	Max	Min	Mean	SD	Max	Min	Mean	SD	Max	Min	Mean	SD
pН		8.3	7.2	7.5	0.2	7.9	7.3	7.6	0.2	8.0	7.5	7.8	0.2
Eh	mV	428	317	381	30	391	354	369	13	398	328	367	26
Т	°C	22.5	21.2	21.8	0.3	22.3	21.3	21.8	0.3	22.4	21.5	21.9	0.3
EC	μS	857	477	563	73	1319	407	810	293	1355	313	652	397
TDS	mg/L	557	310	366	47	857	264	526	190	880	203	423	258
LDO	mg/L	7.0	5.3	6.3	0.6	7.1	6.3	6.8	0.3	7.1	6.6	6.9	0.2
Ca	mg/L	114.5	4.0	70.2	19.7	118.3	28.6	79.4	30.7	88.4	12.9	50.9	30.7
Mg	mg/L	45.1	4.1	24.7	8.3	66.4	17.6	38.1	19.1	74.7	11.4	31.5	25.4
Na	mg/L	117.6	1.1	10.7	26.1	74.9	3.4	27.0	21.5	96.5	4.0	36.6	33.4
К	mg/L	2.4	0.3	0.8	0.4	4.0	0.8	1.3	0.9	2.1	0.5	1.1	0.7
HCO ₃	mg/L	465.7	259.8	341.6	44.7	500.9	252.5	357	80.4	532.1	172.3	311	154.9
SO4	mg/L	99.0	10.6	22.7	18.4	272.2	15.1	81.8	82.2	185.5	14.7	51.8	66.9
CI	mg/L	17.0	4.3	6.6	3.4	98.4	5.7	31.8	30.1	114.1	5.1	31.2	44.3
NO ₃	mg/L	10.6	0.2	3.6	2.8	41.0	1.8	14.0	12.8	23.0	0.1	10.8	7.6
F [.]	mg/L	0.9	0.01	0.1	0.2	2.9	0.1	0.8	0.9	1.4	0.1	0.5	0.5
Li	µg/L	10.0	0.8	2.7	2.5	47.9	2.5	12.2	13.0	25.4	2.6	10.7	7.9
Si	mg/L	11.4	4.5	6.4	1.6	29.0	7.7	13.4	6.0	20.2	9.9	14.3	4.1
В	mg/L	0.3	0.01	0.03	0.1	0.2	0.02	0.1	0.1	0.2	0.01	0.1	0.1
AI	µg/L	10.0	0.7	1.6	1.9	2.7	1.2	1.6	0.4	2.8	1.1	1.8	0.6
Mn	µg/L	4.4	0.3	0.6	1.2	3.6	0.04	0.8	1.2	16.7	0.1	3.9	6.4
Fe	µg/L	69.1	0.2	3.9	14.2	2.3	0.4	1.3	0.6	15.9	0.8	4.4	5.8
Ni	µg/L	8.7	0.1	1.5	1.8	2.3	0.1	1.1	0.7	31.7	0.01	5.4	12.9
Cu	µg/L	1.8	<0.001	0.5	0.5	3.7	<0.001	0.7	1.0	0.9	<0.001	0.2	0.5
Zn	mg/L	1.4	0.02	0.3	0.3	1.2	0.03	0.3	0.3	0.5	0.1	0.2	0.1
Se	µg/L	8.0	0.3	1.1	1.6	2.3	0.3	1.1	0.8	2.4	0.2	0.7	0.9
Sr	mg/L	4.3	0.1	0.4	0.9	26.2	0.3	6.1	8.4	1.9	0.2	1.0	0.5
Cd	µg/L	0.1	0.003	0.02	0.03	0.1	0.002	0.02	0.02	0.02	0.001	0.01	0.01
As	µg/L	1.8	0.2	0.5	0.4	2.1	0.3	1.1	0.5	2.3	0.3	0.9	0.7
Ва	mg/L	0.3	0.02	0.03	0.05	0.18	0.03	0.09	0.06	0.13	0.02	0.05	0.02
Pb	µg/L	1.3	0.02	0.19	0.3	1.7	0.02	0.2	0.5	0.1	<0.001	0.04	0.03
U	µg/L	3.3	0.4	1.3	0.7	3.5	0.6	1.4	0.8	1.9	0.8	1.2	0.4
Na	%	90.5	1.2	8.5	20.6	41.3	2.7	15.8	12.4	49.7	4.4	23.4	16.3
SAR	meq/L	8.4	0.02	0.5	1.8	1.4	0.1	0.6	0.4	1.7	0.1	0.8	0.7
RSC	meq/L	3.7	-1.8	0.1	1.1	1.5	-4.2	-1.3	1.9	2.3	-1.8	0.3	1.4
SSPP	meq/L	62.6	-3.6	3.0	13.1	4.8	0.2	1.1	1.6	2.5	-5.5	-0.2	2.8

* Parameters

Table 5: Basic statistics of the chemical analysis and field parameters of groundwater samples in the three aquifers during wet season (SD means standard deviation, SAR is sodium adsorption ratio, RSC is residual sodium carbonate, SSPP is soluble sodium percentage possible).

Hydrochemistry

Field parameters and major cations and anions for both wet and dry season samples are shown in Tables 5 and 6. The spatial TDS distribution shows that low TDS values and low salinities are found in the northeast and south of the basin and high salinities in the middle part of the basin for the three aquifers according to the groundwater flow from the mountains toward the center of the basin and then to the Greater Zab River (Figures 10 and 11).

The high TDS values in the Shaqlawa-Harrir basin are resulting from the long residence time and enhanced water-rock interaction. In general, TDS and EC in the wet period are lower than in the dry period due to dilution by rainfall in the wet period. The pH of the spring samples increased from the mountains toward the Greater Zab River. The groundwater and surface water samples have pH values ranging between 7 and 8.3 with a mean value of 7.6. The average Ca^{2+} and Mg^{2+} concentrations are 70 mg/L and 26.6 mg/L, respectively. These which are the most abundant cations in the water samples; the average K^+ concentration is very low (about 1.2 mg/L).

The most abundant anion in the water samples is HCO_3^- . In groundwater generally most of the hydrogen carbonate ions are derived from the carbon dioxide in the atmosphere, soil gas and the dissolution of carbonate rocks. The average hydrogen carbonate concentration of the samples, calculated according to TIC and pH by using PHREEQC program, is 305 mg/L. Sulfate comes from the atmosphere and from the dissolution of sulfate minerals in the sedimentary rocks. Shales also may release a large amount of sulfate through the oxidation of marcasite and pyrite. The average SO_4^{-2} concentration of 34.6 mg/L is rather moderate. The most important of the Cl sources in the near-surface water seems to be chloride transported in the atmosphere and subsequently falling to earth by rain or snow. The average chloride concentration is 16.5 mg/L. Most nitrates in natural water originate from organic sources or from industrial and agricultural activities; the average concentration in the samples is 10 mg/L (Figures 12 and 13).

Por*	Unit		Fissured-ka	irstic aquifer			Karstic	aquifer			Porous	aquifer	
Fai	Offic	Max	Min	Mean	SD	Max	Min	Mean	SD	Max	Min	Mean	SD
pН		8.1	7.3	7.6	0.2	8.2	7.1	7.6	0.3	7.9	7.5	7.7	0.2
Eh	mV	444	374	417	15	449	399	421	18	426	398	411.2	10
Т	°C	27.8	26.4	27.2	0.4	27.7	26.9	27.4	0.2	27.6	27.1	27.5	0.2
EC	μS	711	458	546	56	1382	422	741	312	2190	325	787	716
TDS	mg/L	462	297	355	37	898	274	482	203	1423	211	511	465
LDO	mg/L	7.5	7.2	7.4	0.1	7.5	5.6	6.9	0.6	7.8	6.7	7.3	0.4
Ca	mg/L	96.5	14.9	74.2	15.4	173.0	28.4	81.4	41.1	94.0	24.6	54.4	30.0
Mg	mg/L	38.6	12.8	24.2	5.8	53.9	15.2	31.5	15.1	84.1	12.8	31.9	28.2
Na	mg/L	88.7	0.2	5.7	18.1	48.6	2.2	21.8	16.9	239.2	3.6	61.0	89.0
К	mg/L	1.2	0.4	0.7	0.2	1.7	0.7	1.1	0.4	2.7	0.4	1.3	0.9
HCO ₃	mg/L	415.6	263.8	311.8	32.5	374.3	194.0	284.3	55.2	393.7	172.8	269.8	90.6
SO4	mg/L	32.6	3.9	10.2	5.6	280.8	5.1	73.2	86.8	99.6	6.6	29.9	35.9
CI	mg/L	15.8	1.7	3.2	2.9	80.2	2.3	20.9	24.8	398.8	2.3	76.6	159
NO ₃	mg/L	10.9	1.1	4.4	2.7	27.0	3.8	10.3	7.2	27.4	10.3	15.1	7.0
F⁺	mg/L	1.0	0.03	0.13	0.2	1.9	0.1	0.7	0.6	1.2	0.1	0.5	0.4
Li	µg/L	12.4	0.8	2.4	2.5	18.1	1.9	9.6	6.1	22.5	3.0	9.7	7.1
Si	mg/L	11.0	4.0	5.6	1.8	13.8	5.7	9.9	2.8	13.3	9.1	10.7	1.8
В	mg/L	0.1	0.01	0.02	0.03	0.1	0.01	0.1	0.03	0.2	0.01	0.1	0.1
AI	µg/L	18.0	0.9	2.9	3.7	3.9	1.0	1.7	0.8	3.0	1.3	1.9	0.6
Mn	µg/L	5.8	<0.001	0.7	1.3	3.0	0.01	0.9	1.0	13.9	0.2	4.7	6.7
Fe	µg/L	300.5	1.3	17.3	61.9	7.9	1.3	3.2	2.0	3.2	2.2	2.6	0.4
Ni	µg/L	6.6	0.03	1.7	1.7	2.7	0.3	1.3	0.8	52.2	0.04	8.8	21.3
Cu	µg/L	1.7	<0.001	0.2	0.5	2.3	<0.001	0.6	0.7	0.4	<0.001	0.01	0.3
Zn	mg/L	1.0	0.01	0.2	0.3	2.6	0.01	0.4	0.8	0.2	0.001	0.1	0.1
Se	µg/L	2.8	0.3	0.9	0.7	1.5	0.2	0.7	0.5	2.7	0.03	0.7	1.0
Sr	mg/L	4.0	0.1	0.4	0.8	12.9	0.2	5.2	5.0	1.7	0.3	0.9	0.5
Cd	µg/L	0.1	0.002	0.03	0.04	0.1	0.002	0.001	0.003	0.003	<0.001	0.01	0.01
As	µg/L	2.9	0.1	0.7	0.7	2.1	0.3	0.9	0.6	1.9	0.2	0.8	0.6
Ва	mg/L	0.3	0.02	0.04	0.1	0.2	0.02	0.1	0.1	0.1	0.02	0.05	0.04
Pb	µg/L	0.9	0.04	0.2	0.2	0.4	0.04	0.1	0.1	0.2	0.03	0.1	0.1
U	µg/L	4.6	0.6	1.3	1.0	3.5	0.7	1.4	0.8	2.0	0.6	1.2	0.5
Na	%	66.8	0.3	4.5	13.6	40.1	2.2	16.5	13.6	47.4	3.4	26.1	18.1
SAR	meq/L	3.3	0.001	0.2	0.7	1.3	0.05	0.5	0.4	3.6	0.1	1.2	1.3
RSC	meq/L	2.5	-2.2	-1.1	0.9	0.8	-7.9	-2.0	2.6	1.0	-5.2	-1.1	2.2
SSPP	meq/L	2.8	-0.6	0.2	0.6	1.9	0.1	0.6	0.7	1.9	0.1	0.9	0.6

* Parameters

Table 6: Basic statistics of the chemical analysis and field parameters of groundwater samples in the three aquifers during dry season (SD means standard deviation, SAR is sodium adsorption ratio, RSC is residual sodium carbonate, SSPP is soluble sodium percentage possible).

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Figure 10: Distribution of total dissolved solids (TDS) and pH of the water samples from the three aquifers; (A) fissured-karstic aquifer; (B) karstic aquifer; (C) porous aquifers.



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Most groundwater samples were classified as to be of Ca-Mg-HCO₃ and Mg-Ca-HCO₃ type; only five well-water samples belong to the Na-Ca-HCO₃ type. The physicochemical parameters for all the samples suggested that the groundwater is generally good for domestic use, irrigation and industrial purposes (Tables 7 and 8).

The relationship between the Na⁺ and Cl⁻ concentrations has been used to identify the form of salinity [23-25]. The high concentration of Na⁺ and Cl⁻ detected in water sample 37 in porous aquifer during dry season proposes the dissolution of chloride in the form of halite (Figure 14).

			_			Cations	s (mg/L)		Anions (mg/L)				
SN	Water type	рН	pE	EC (µS)	Na	К	Mg	Са	CI	NO ₃	SO₄	HCO ₃	
1	Ca-Mg-HCO	7.2	6.1	632	2.2	0.8	33.1	80.4	10.1	1.9	30.4	399.7	
2	Ca-Mg-HCO ₃	7.4	7.1	577	1.9	0.7	32.4	74.0	5.0	0.7	17.0	372.0	
3	Ca-Mg-HCO ₃	7.3	6.5	564	2.2	0.8	29.2	75.1	5.5	1.5	17.1	352.1	
4	Ca-Mg-HCO ₃	7.4	6.5	516	20.5	1.1	28.0	66.8	5.1	2.1	15.8	332.7	
5	Ca-Mg-HCO ₃	7.5	6.4	545	1.8	0.7	26.4	75.8	4.9	2.1	14.6	347.2	
6	Ca-Mg-HCO ₃	7.5	6.5	560	1.7	0.5	28.4	76.1	4.9	4.2	16.0	347.1	
7	Ca-Mg-HCO ₃	7.4	6.3	540	1.7	0.7	26.7	74.0	4.8	2.0	15.5	349.7	
8	Ca-Mg-HCO ₃	7.4	6.3	559	1.5	0.6	20.5	61.1	4.7	2.6	16.9	290.6	
9	Mg-Ca-HCO ₃	7.4	6.5	556	1.8	0.8	28.8	19.0	4.8	1.7	17.8	201.4	
10	Ca-Mg-HCO ₃	7.5	6.8	546	1.6	0.7	21.7	65.5	4.6	1.2	20.2	313.4	
11	Ca-Mg-HCO ₃	7.7	6.5	568	1.1	0.5	18.3	71.7	4.3	1.4	17.2	315.3	
12	Na-Ca-Mg-HCO ₃	7.5	5.7	547	56.2	2.4	7.2	39.0	5.9	1.2	21.4	301.9	
13	Ca-Mg-HCO ₃	7.3	6.5	720	5.6	0.9	38.9	88.7	13.9	4.1	51.9	416.3	
14	Ca-Mg-HCO ₃	7.5	5.7	642	2.7	0.3	30.9	90.6	13.6	7.1	33.5	410.5	
15	Ca-Mg-HCO ₃	7.7	5.7	515	1.6	0.6	26.0	70.3	4.8	1.7	16.8	339.9	
16	Mg-Ca-Na-HCO ₃	7.5	6.2	887	36.3	1.8	49.9	80.1	50.2	6.2	51.7	482.9	
17	Ca-Mg-HCO ₃	7.8	6.5	565	3.4	0.8	24.9	78.3	6.4	6.6	15.6	353.4	
18	Ca-Mg-HCO ₃	7.6	6.5	561	3.7	0.9	25.9	78.8	5.9	1.2	18.0	374.9	
19	Ca-Mg-HCO ₃	7.6	6.2	542	3.2	0.7	23.6	78.5	5.7	2.8	15.7	352.0	
20	Ca-Mg-HCO ₃	7.5	6.6	532	2.3	0.4	24.4	75.1	5.1	7.5	13.1	308.8	
21	Mg-Ca-HCO3	7.9	6.4	962	18.7	1.1	66.4	56.7	40.3	29.3	42.9	350.4	
22	Ca-Mg-HCO ₃	7.6	6.6	477	2.3	0.5	18.4	72.7	5.2	6.7	12.4	313.6	
23	Ca-Mg-HCO ₃	7.8	6.9	504	2.6	0.6	21.2	73.8	5.6	6.9	12.7	330.7	
24	Ca-Mg-HCO ₃	7.6	7.1	550	2.9	0.7	27.4	74.2	5.8	5.9	16.7	366.8	
25	Ca-Mg-HCO ₃	7.9	6.8	537	3.7	0.7	25.2	73.8	6.2	10.6	19.9	338.2	
26	Mg-Ca-HCO3	7.8	6.7	496	9.9	1.9	21.1	29.6	9.4	14.1	16.5	200.1	
27	Ca-Mg-HCO ₃	7.8	6.8	412	4.8	0.3	11.4	62.3	7.5	34.4	26.1	195.9	
28	Ca-Mg-HCO ₃	7.8	6.7	501	4.0	0.5	11.4	62.6	5.7	23.0	21.0	225.8	
29	Ca-Mg-HCO ₃	7.7	6.6	594	7.4	1.4	20.3	84.7	9.1	27.7	40.6	310.1	
30	Na-SO ₄ -HCO ₃	8.3	5.9	550	117	0.9	4.1	4.0	17.0	0.2	46.9	259.8	
31	Ca-Mg-HCO ₃	8.1	6.4	297	2.9	0.6	8.8	45.5	4.5	3.1	19.3	168.9	
32	Ca-Mg-HCO ₃	7.9	6.6	514	4.5	0.8	22.1	75.7	6.1	24.3	19.5	288.3	
33	Mg-Ca-Na-HCO ₃	7.9	6.7	400	29.5	0.9	21.6	25.8	5.1	11.2	14.7	234.2	
34	Ca-Mg-HCO ₃	7.6	6.1	606	13.2	1.5	23.6	74.9	20.5	41.0	28.6	269.8	
35	Ca-Mg-HCO ₃	7.6	5.4	546	3.4	0.8	26.4	74.5	5.6	6.6	20.6	340.4	
36	Ca-Mg-HCO ₃	7.7	6.2	481	4.0	0.5	17.6	67.4	5.4	27.6	18.5	273.4	
37	Mg-Ca-Na-SO ₄ -HCO ₃	7.6	5.5	1355	96.5	2.1	74.7	88.4	114	0.1	185.5	532.1	
38	Ca-Mg-Na-HCO ₃	7.6	5.9	652	24.1	5.6	29.5	55.3	28.3	<0.01	37.0	330.7	
39	Mg-Ca-Na-HCO ₃	7.9	6.0	407	33.5	1.0	18.3	29.7	5.9	4.1	15.1	252.5	
40	Ca-Mg-HCO ₃	7.9	6.9	609	5.7	0.3	20.6	41.4	5.6	40.9	16.2	200.8	
41	Na-Mg-Ca-HCO ₃	8	5.9	455	44.8	1.1	16.5	12.9	6.4	10.5	21.6	215.6	
42	Ca-Mg-HCO ₃	7.9	6.2	313	8.2	0.5	14.6	35.4	5.6	13.7	16.4	1/2.3	
43	Na-Mg-Ca-HCO3	7.9	6.0	448	46.0	0.8	17.6	28.6	5.7	8.8	18.1	266.5	
44	Ca-Mg-SO ₄ -HCO ₃	7.6	6.4	8//	28.7	0.8	32.8	93.2	45.2	13.5	110.8	351.3	
45	$Ca-Mg-SO_4-HCO_3$	7.4	6.4	1011	22.1	1.1	54.2	118	35.1	11.2	1/2.8	450.7	
40	Ca-Mg-Na-SO ₄ -HCO ₃	7.5	6.3	1109	43.0	1.2	60.3	103	69.7	5.9	131.0	500.9	
4/	$Ca-Mg-Na-SO_4-HCO_3$	7.4	b.U	1319	/4.9	4.0	61.9	11/	98.4	1.8	272.2	408.2	
40		7.3	7.1	528	1.30	0.67	22.0	52.7	4./1	3.92	10.6	285.5	
49		7.4	7.2	00/	9.09	0.98	45.1	07.0	13.1	4.34	90.9	405./	
50	Ca-Mg-HCO3	1.4	7.3	541	4.58	8.26	7.0	87.2	8.39	41.5	18.8	2/4./	

*Sample number

Table 7: Chemical analysis, field parameters, and water type for the water samples taken during wet season.

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Conclusions

The present study examined the stable isotopes and radiocarbon in groundwater from the three main aquifers in the Shaqlawa-Harrir basin. The fissured-karstic aquifer was more depleted in heavy isotopes than the karstic aquifer, while the porous aquifer is enriched. The water vapor source in the area originated from two sea cyclones;

		рН	Cations (mg/L)					Anions	Anions (mg/L)			
SN	Water type	pН	рE	EC (µS)	Na	К	Mg	Са	CI	NO ₃	SO,	HCO ₃
1	Ca-Mg-HCO	7.3	6.3	643	1.6	0.7	31.6	77.4	2.3	2.5	10.3	350.8
2	Ca-Mg-HCO	7.4	7.1	581	1.8	0.8	30.4	70.5	2.5	1.1	10.1	324.3
3	Ca-Mq-HCO	7.5	7.1	568	1.9	0.9	27.1	72.7	2.8	1.6	9.8	310.5
4	Ca-Mg-HCO	7.5	6.8	538	1.7	0.8	26.0	64.9	2.3	2.6	8.2	291.1
5	Ca-Mq-HCO	7.5	6.9	536	1.5	0.6	23.3	72.7	2.0	3.0	8.5	294.4
6	Ca-Mg-HCO,	7.5	6.8	555	1.4	0.5	26.2	71.6	2.2	4.8	8.7	308.1
7	Ca-Mg-HCO,	7.6	6.8	519	1.4	0.7	25.0	70.9	2.1	2.5	8.0	295.3
8	Ca-Mg-HCO	7.6	7.0	487	0.5	0.6	20.3	86.6	2.0	3.1	9.4	320.4
9	Ca-Mq-HCO	7.5	7.1	516	0.8	0.8	23.4	67.5	2.0	2.1	10.1	282.3
10	Ca-Mg-HCO,	7.5	7.0	523	0.7	0.8	23.2	69.8	1.8	1.8	9.8	282.8
11	Ca-Mg-HCO,	7.5	7.0	510	0.2	0.4	19.5	91.7	1.7	1.6	9.8	330.1
12	Ca-Mq-HCO	7.4	7.1	479	2.5	0.7	12.8	82.3	1.9	1.8	8.7	332.6
13	Ca-Mg-HCO	7.6	6.9	663	3.9	0.7	36.5	74.9	5.7	3.8	29.8	339.5
14	Ca-Mg-HCO	7.4	7.0	620	1.7	0.4	30.7	90.5	6.2	6.6	12.8	358.4
15	Ca-Mq-HCO	7.6	7.1	458	1.3	0.5	25.4	69.2	2.0	1.8	8.9	299.1
16	Ca-Mq-Na-HCO	7.5	6.9	901	39.4	1.9	44.6	74.9	49.7	10.3	34.4	372.3
17	Ca-Mg-HCO	7.7	6.8	520	2.4	0.8	24.5	71.7	4.2	8.3	8.1	290.6
18	Ca-Mg-HCO	7.5	7.0	558	3.3	0.9	25.3	77.1	3.2	3.1	10.4	322.1
19	Ca-Mg-HCO	7.6	7.0	508	2.9	0.7	23.5	77.8	3.0	3.2	8.2	315.5
20	Ca-Mg-HCO	7.6	6.8	540	2.0	0.5	24.2	74.3	2.4	9.3	5.7	297.9
21	Ca-Mg-HCO	7.7	6.8	476	2.2	0.7	15.2	71.6	2.3	8.8	5.1	264.6
22	Ca-Mg-HCO	7.6	7.3	484	2.0	0.5	18.0	71.5	2.4	7.9	5.0	263.8
23	Ca-Mg-HCO	7.6	7.4	525	2.3	0.6	21.0	73.2	2.9	7.4	5.3	285.9
24	Ca-Mg-HCO	7.6	7.2	536	2.2	0.7	26.4	73.1	2.3	5.2	7.7	312.5
25	Ca-Mg-HCO	7.7	7.2	498	3.2	0.7	25.2	73.8	3.5	10.9	12.3	295.7
26	Ca-Mq-HCO	7.8	7.1	519	13.3	3.1	26.4	48.1	13.0	28.1	25.8	222.4
27	Ca-Mq-SO,-HCO	7.8	7.2	877	20.5	8.9	17.2	116.6	41.2	17.6	98.2	253
28	Ca-Mg-HCO	7.8	7.2	457	3.6	0.5	12.8	73.3	3.8	27.4	23.3	227.9
29	Ca-Mg-HCO,	7.6	7.2	537	6.5	1.4	17.1	76.9	4.4	4.0	25.0	266.2
30	Na-Mg-HCO,	8.1	7.4	583	88.7	1.2	14.5	14.9	15.8	5.3	32.6	270.4
31	Ca-Mg-SO ₄ -HCO ₃	8.0	7.1	480	6.2	1.1	17.3	60.7	4.5	2.0	56.7	196.3
32	Ca-Mg-HCO	8.0	6.9	425	4.5	0.7	21.3	50.1	4.5	30.3	22.2	194.2
33	Mg-Na-Ca-HCO ₃	7.9	7.0	406	28.7	0.9	20.3	24.6	2.3	12.9	6.6	215.3
34	Ca-Mg-Na-SO ₄ -HCO ₃	7.6	7.1	681	35.5	1.7	22.4	55.7	46.9	27.0	69.6	194
35	Ca-Mg-HCO ₃	7.6	7.1	570	3.1	0.8	25.4	71.6	2.9	7.2	12.2	289.5
36	Ca-Mg-HCO ₃	7.7	7.2	473	4.2	0.5	17.9	72.9	3.6	33.5	20.8	232.4
37	Na-Mg-Ca-HCO ₃	7.5	6.7	2190	239	2.7	84.1	94.0	398	<0.01	99.6	393.7
38	Ca-Mg-Na-HCO ₃	7.7	6.9	660	24.2	5.8	28.7	64.1	22.3	0.5	13.0	306
39	Na-Mg-Ca-HCO ₃	8.2	6.7	422	33.4	1.0	17.6	28.6	3.1	4.4	7.4	226.4
40	Ca-Mg-HCO ₃	7.7	7.4	533	4.9	0.2	15.5	73.0	5.1	41.9	22.9	237.4
41	Na-Mg-Ca-HCO ₃	7.8	6.8	443	47.7	1.1	16.1	24.6	2.5	11.2	6.6	237.1
42	Ca-Mg-HCO ₃	7.8	7.1	325	7.7	0.4	13.6	34.7	2.7	13.8	9.1	172.8
43	Na-Mg-Ca-HCO ₃	7.7	6.9	466	43.5	0.8	17.4	28.4	2.8	10.7	9.8	241
44	Ca-Mg-HCO ₃ -SO ₄	7.3	7.4	1382	48.6	1.4	44.5	173	80.2	12.5	304.1	267.6
45	Ca-Mg-SO ₄ -HCO ₃	7.3	7.5	1056	21.7	1.5	53.9	117.5	31.0	19.7	147.2	346.4
46	Ca-Mg-SO ₄ -HCO ₃	7.3	7.4	924	17.3	1.0	48.9	91.6	19.0	6.9	77.3	374.3
47	Ca-Mg-SO ₄ -HCO ₃	7.1	7.6	1034	24.5	1.5	48.1	105.6	30.6	7.5	145.4	316.8
48	Ca-Mg-HCO ₃	7.5	7.5	545	1.0	0.8	16.9	88.9	2.6	5.2	3.9	319.8
49	Ca-Mg-HCO ₃	7.8	7.3	711	4.4	0.9	38.6	96.5	4.4	5.0	17.1	415.6
50	Ca-Mg-HCO ₃	7.6	7.4	539	3.3	7.4	8.3	87.8	7.3	40.5	22.9	233.7

* Sample number

Table 8: Chemical analysis, field parameters, and water type for the water samples taken during dry season.



Figure 14: Relation between Na* and C⁻ for deep well samples; (A) wet season & (B) dry season, spring and river samples (C) wet season & (D) dry season.

Mediterranean Sea and Persian Gulf. More negative isotopic signature along the southwestern border (Safin and Pirmam Mountain) and eastern part (Harrir Mountain) in comparison to the northern part of the basin indicates the altitude effect on the isotopic composition.

According to ¹⁴C analysis the recharge in the area occurs in the Safin and Pirmam mountains in the south and southwest and the Harrir Mountain in the eastern part of the basin. Hydrochemical investigations indicated that the high TDS values of the groundwater in the Shaqlawa-Harrir basin result from a long residence time and enhanced water-rock interaction. The type of the water samples is mainly hydrogen carbonate and the water quality is generally suitable for drinking, agriculture, irrigation, and industrial purposes.

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