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HYDROCHEMICAL AND ENVIRONMENTAL ASSESSMENT OF GROUNDWATER AT THE IRAQI PART OF THE LESSER ZAB RIVER BASIN, NORTHEAST-IRAQ

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ABSTRACT

A total of eighteen groundwater samples and two spring samples were collected from the Iraqi part of the Lesser Zab River Basin (LZRB) and analyzed for physicochemical parameters major, minor, nutrients ions, and trace elements as Si, Fe, Al, Mn, Li, Sr, Br, Ba, B, Pb, Zn, Cr, V, Cu, Co, Ni, As, Se, Mo, Cd, Sb, and U. The chemical analyses show that the groundwater of the LZRB is alkaline, and the Ca^{2+}, Mg^{2+}, HCO_3^-, and SO_4^{2-} are the major contributing ions, and the NO_3^- is the major nutrient. The major governing factors of groundwater chemistry in the basin are rock weathering, dissolution/precipitation of minerals, and ion exchange. Based on international and Iraqi water quality standards, all groundwater samples are undrinkable for a human being. Whereas, Pb exceeds the standard limit for most samples. Some other water quality parameters are exceeding the prescribed limits for some samples. Based on relevant parameters and classification, all samples are suitable, with certain qualifications, for irrigation and livestock watering.

التقييم الهيدروكيميائي والبيئي للمياه الجوفية في الجزء العراقي من حوض نهر الزاب الصغير، شمال شرق العراق

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و قصي عبد الوهاب السهيل

المستخلص

تم جمع ثمانية عشر عينة من المياه الجوفية وعينتين من مياه العيون من الجزء االعراقي لحوض نهر الزاب الصغير وتحليل الخصائص الفيزيوكيميائية، الايونات الرئيسية، الثانوية، المغذيات والعناصر الأثرية لها (Si, Fe, Al, Mn, Li, Sr, Br, Ba, B, Pb, Zn, Cr, V, Cu, Co, Ni, As, Se, Mo, Cd, Sb, and U). المياه الجوفية لحوض نهر الزاب الصغير ذات طبيعة قلوية وايونات الكالسيوم والمغنيسيوم والبايكاربونات والكبريتات هي الايونات الرئيسية ويعتبر ايون النترات هو المغذي الرئيس. العوامل الرئيسية التي تحكم كيمياء المياه الجوفية في الحوض هي تجوية الصخور، واذابة/ ترسيب المعادن وتبادل الأيونات. وفقا للمعايير المحلية والعالمية، فإن المياه الجوفية للعينات المدروسة تعد غير صالحة لشرب الإنسان حيث يزيد تركيز الرصاص عن الحد الطبيعي لمعظم العينات. وهناك ايضا بعض المتغيرات النوعية للمياه تزيد عن الحدود المسموحة لشرب الانسان لبعض العينات. من ناحية اخرى اظهرت نتائج تقييم نوعية المياه ان المياه الجوفية للابار المدروسة ملائمة للري وشرب المواشي.

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INTRODUCTION

Water with good quality and sufficient quantity of different resources is a strategic factor for our quality of life and the economic development of a country. The groundwater of the Lesser Zab River Basin (LZRB) is the main source of daily human consumption, agricultural uses, and other anthropogenic activities. The study area is distinguished by the presence of vast agricultural lands as well as many cities and towns. Thus, major, minor, nutrients ions, and trace elements were evaluated to determine the main hydrogeochemical characteristics of groundwater.

Groundwater assessments are achieved based on several factors; quality of source water, precipitation, lithology, land use and land cover activities, and subsurface geochemical processes (Lerner and Harris, 2009; Jalees *et al*., 2020). The urbanization in the LZRB as a part of the Kurdistan region has been expanding quickly in the last decades (Al-Saady *et al*., 2015). Basically, the groundwater of LZRB and its surrounding area is the main source of water supply for urban and built-up land. Land use development of the LZRB as urban expansion and agricultural activities led to an increase in groundwater requests during recent decades (Al-Saady *et al*., 2015). This led to a substantial and serious load on the groundwater quality and quantity with a substantial risk to the preservation of groundwater quality. Furthermore, the absence of a sewage network in most cities and towns results in wastewater being released to the surface and groundwater resources. Lithology and land use activities in a region are considered the main factor responsible for variation in the physicochemical variables of groundwater (Schiavo *et al*., 2006; Magesh and Chandrasekar, 2013; Prasanth *et al*., 2012).

Groundwater is the primary source of water for drinking and agricultural purposes in most regions of the basin. Accurate information on the quality and quantity of groundwater is essential for developing and managing groundwater supplies in the LZRB. Therefore, the groundwater samples result will contribute to evaluating the influence of Land Use and Land Cover (LULC) on the groundwater; identifying regional and spatial variation of water chemistry, and environmental risk assessment of contamination status. An attempt has also been carried out to determine hydrochemical facies and classifies the groundwater based on different classification schemes. In addition, evaluating the groundwater quality for different purposes was also achieved.

STUDY AREA

The LZRB is located in the NE part of Iraq and NW of Iran between latitudes 35° 10' – 36° 55' N and longitudes 43° 25' – 46° 20' E (Fig.1). The basin area covers about 20,000 Km^2 where the major portion of 70.7% in Iraq and its catchment area extends partly to 29.3% in Iran (Al-Saady *et al*., 2015). The topography of the basin displays gradual variance from complex mountains in the north to flat terrain, hills, and undulated plains in the south. The highest altitude value is 3578 meters above sea level (masl), while the minimum elevation value is 86 masl at the confluence with the Tigris in the southwestern part. The total length of the LZR, which flows from the meeting point of the main tributaries, Nirawan valley and Hami Qeshan, in the highlands of Iran and Iraq territories into the Tigris River is 374 Km (Al-Saady *et al*., 2015). It is supplied by water from ice melting and rainfall causing high discharge in spring and low discharge in summer. The LZRB climate is warm temperate in the middle and upper parts, and arid in the lower part, with hot dry summers, and relatively short spring and fall seasons compared to summer and winter (Al-Saady *et al*., 2016).

Climate data of the LZRB are collected from four meteorological stations distributed in the upper, middle, and lower parts of the main basin involving Penjwin, Koya, Dokan, and Kirkuk stations. The air temperature rises during the summer season and falls during winter. The lowest mean monthly air temperature for all stations is 6.2 ºC, which was recorded in January, and the highest mean monthly air temperature is 33.3 ºC recorded in July. The lowest mean monthly relative humidity for all station stations was 30.9% recorded in July and the highest mean monthly relative humidity 69.4% was recorded in January. The annual total precipitation of the four selected stations is 604 mm representing the whole basin. The highest mean monthly precipitation for all stations was 139.3 mm, which was recorded in January. The minimum and maximum mean monthly evaporation of all stations are 41.4 mm and 374.2 mm, which were recorded in January and July, respectively.

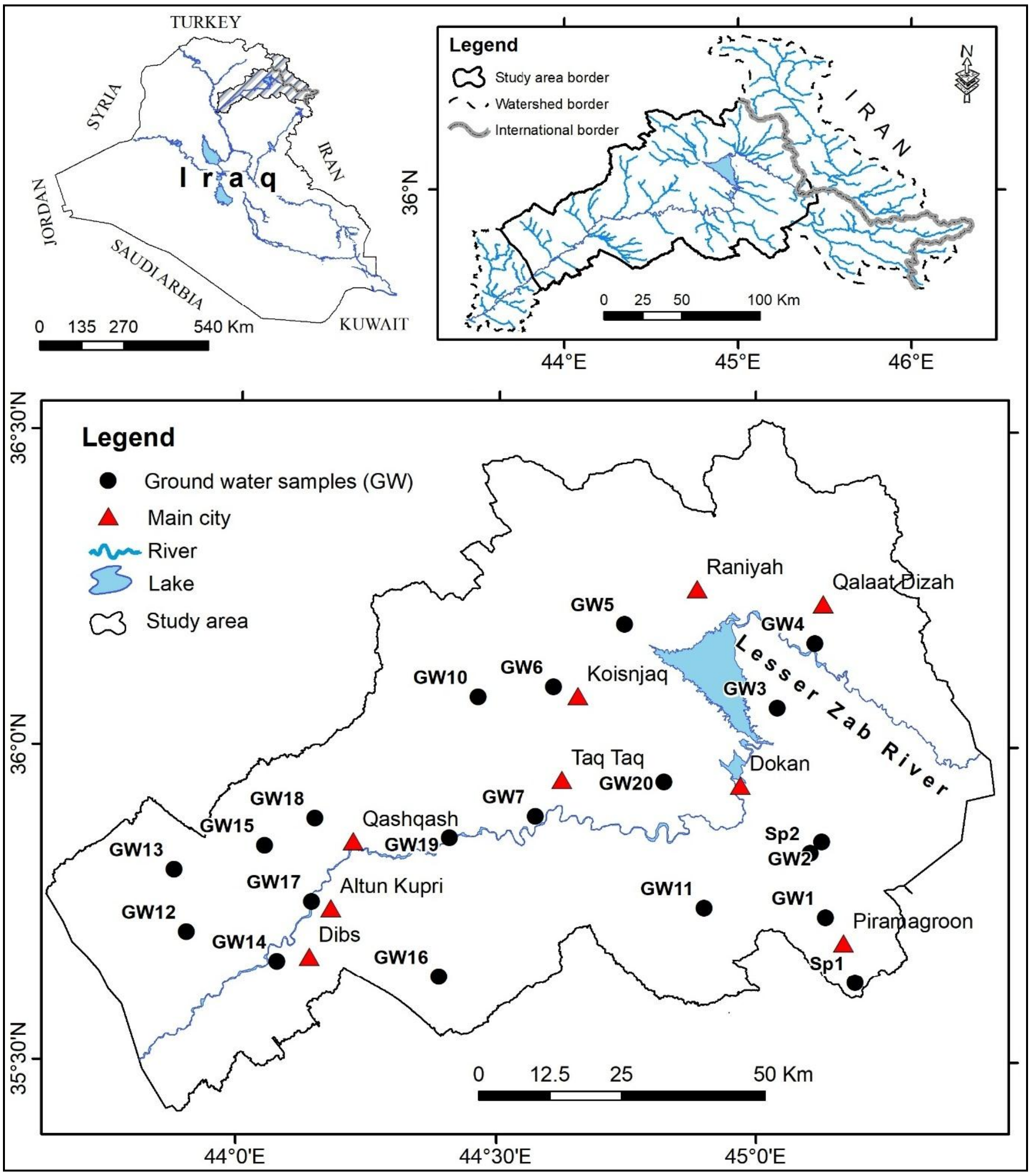

Fig.1: Location map of the study area. The Upper left map of Iraq shows borders with neighboring countries and the study area. The upper right map shows the drainage pattern of the LZRB in Iraq and Iran. Lower part location map of the study area with the main cities and location of samples

The LZRB, between its riverhead (in northwest Iran and northeast Iraq) and the river mouth at the meeting point with the Tigris River, drains a wide range of different lithostratigraphic units ranging in age from the Precambrian to Quaternary sediments (Nezhad, 1973; Houshmandzadeh, 1974; Sissakian, 1992; Sissakian, 1998; Ma’ala, 2007; and Jassim and Goff, 2006). These units consist dominantly of different types of igneous, metamorphic, and sedimentary rocks in the upper parts and sedimentary rocks, mostly carbonate in the middle part and detritus in the lower part (Ma’ala, 2007; Sissakian, 1998) as shown in (Fig.2).

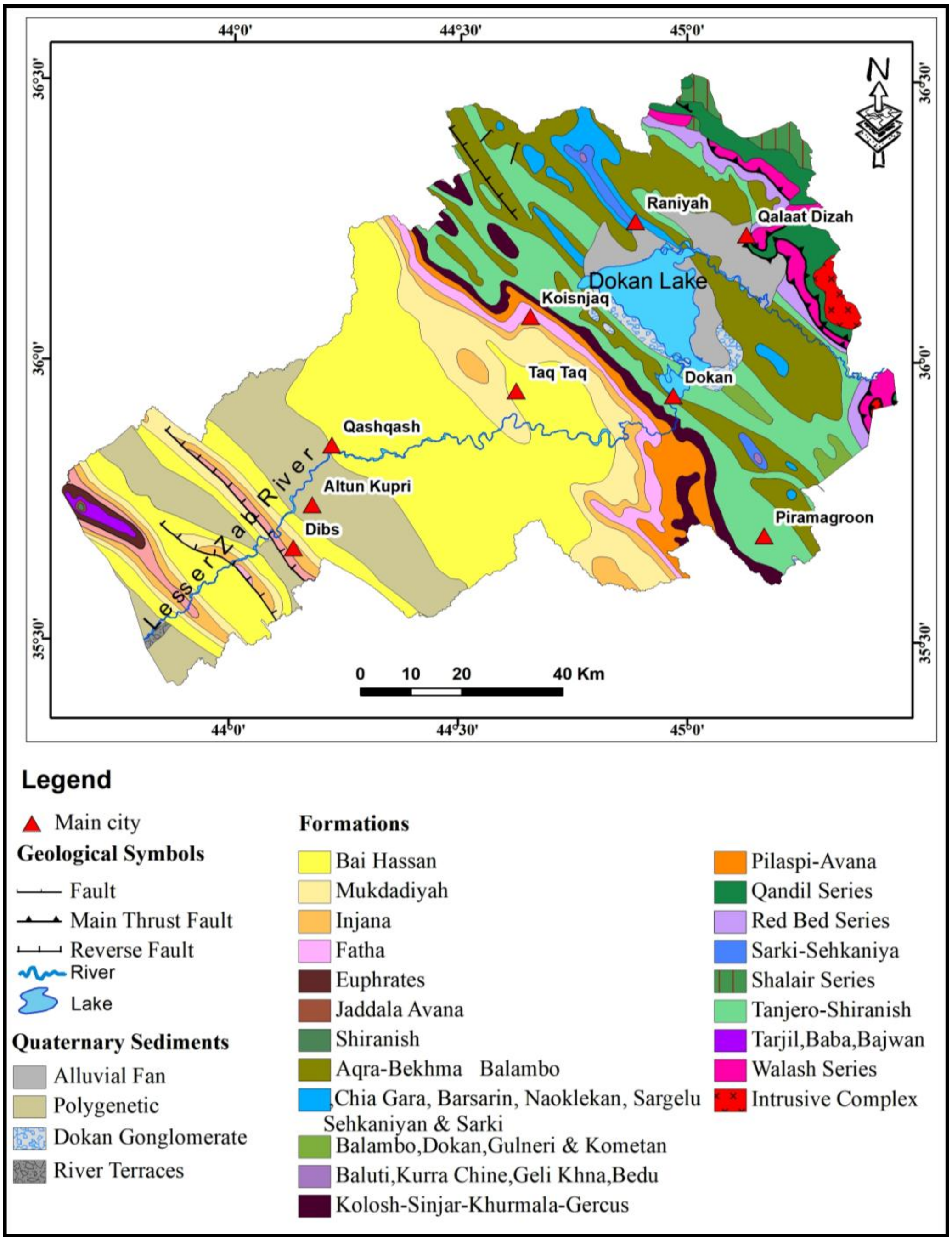

Fig.2: Geological map of the study area (Sissakian and Fouad, 2015)

Clastics sedimentary rock as the Bai Hassan and Mukdadiyah formations are the main water-bearing formations in the middle and lower part of the LZRB, as well as the Injana Formation and Quaternary sediments (Al-Jiburi and Al-Basrawi, 2012). The general direction of groundwater in the study areas is from the upper part towards the main course of the river, with the presence of another movement in the lower part towards the southwest (Fig.3).

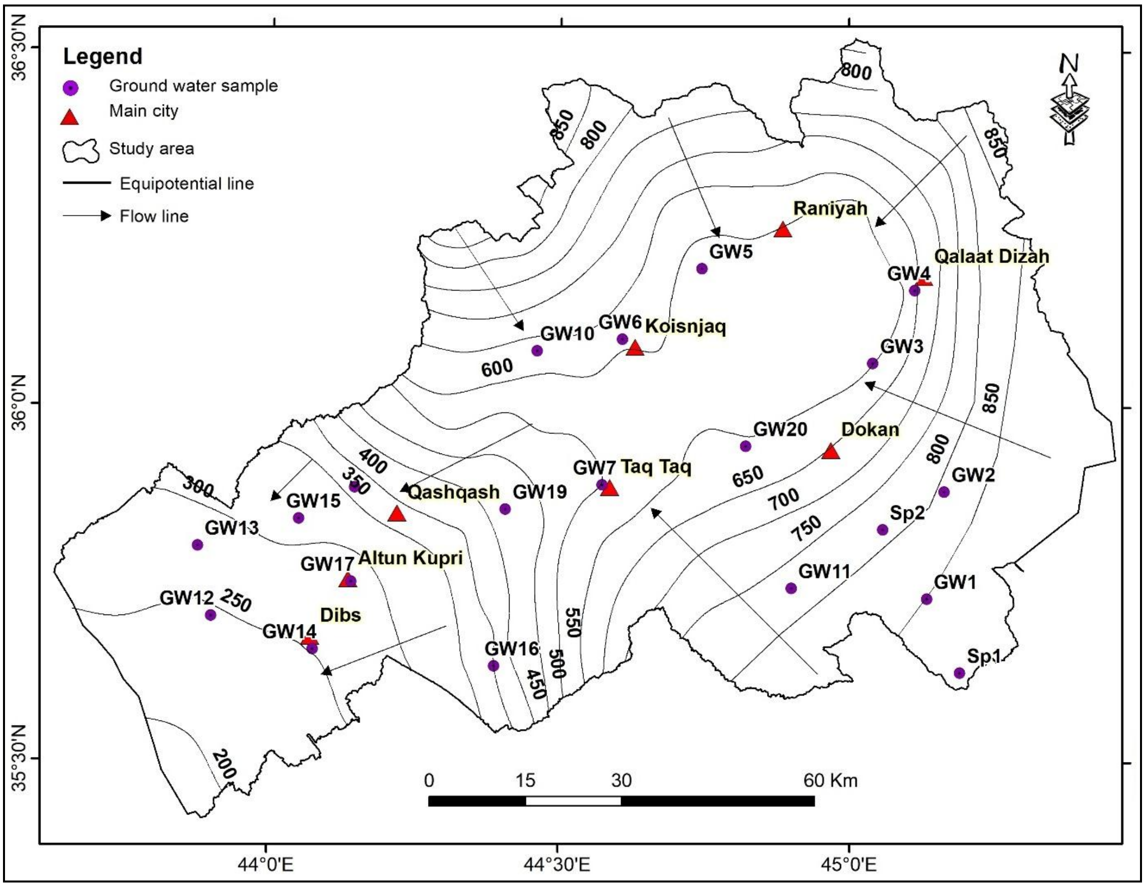

Fig.3: Equipotential lines and regional groundwater flow direction map of the LZRB aquifers (Al-Jiburi and Al-Basrawi, 2015)

- **Land Use and Land Cover (LULC) of the LZRB**

The LZRB is characterized by different LULC classes as an urban area, water body, agriculture and natural vegetation, and barren land (Al-Saady *et al*., 2015; Al-Saady *et al*., 2016). The Middle and lower parts of the LZRB are characterized by higher land use activities, such as agricultural land, and many cities, and rural communities relative to the upper part. Discharge of wastewater directly into river courses mostly without any treatment represents an important source of pollution for surface and groundwater. Manure of livestock and poultry farms, which are widely spread in the middle and lower part of the basin also is considered an important source of pollution.

SAMPLING AND METHODOLOGY

Twenty sites were chosen to collect groundwater samples during April 2014 (wet season) mainly from unconfined aquifer wells to monitor the variations in the physicochemical characteristics and hydrochemistry of major, minor ions, and trace elements at the Iraqi part of the LZRB (Fig.1). Seven groundwater samples were collected from the Quaternary sediments' aquifer. The groundwater well samples and two spring samples were collected from geological formations of different ages and environments, which consist mainly of clastic rocks such as the Mukdadiyah, Bai Hassan, and Injana formations (Sissakian, 1998; Ma'ala, 2007). Only two samples were collected from the carbonate rocks of the Pilaspi and Chia Gara formations, while two spring samples were collected from the carbonate rocks of the Tanjero and Kolosh formations. The sampling sites of selected groundwater wells were used mainly for drinking and irrigation. Eighteen groundwater samples from wells of the shallow aquifer and two samples from springs were collected in prewashed polyethylene bottles. Groundwater samples were chosen by dividing the main basin into equal grid cells and each sample is collected randomly within each cell depending on variation in LULC categories.

All samples were filtered using 0.45 µm pore size filters to separate suspended materials. Sample bottles were rinsed with filtered water from the same sample water before sampling. There are five samples were collected from each site for different analysis as follow; **1)** unfiltered samples for total suspended solids (TSS) analysis, **2)** 500 ml of unfiltered samples by adding 50 ml of zinc acetate and shaking in the field for hydrogen sulfide analysis (H_2S), **3)** filtered unacidified samples for major and minor ions analysis, and **4)** filtered unacidified samples for dissolved organic carbon (DOC) analysis.

- **Analytical techniques**

All these samples were stored in a cool box at a temperature of 4 °C and immediately transferred to the laboratories of GEOSURV-Iraq and Freiberg University of Mining and Technology in Germany. A portable multi-parameter WTW Multi 3430-type was calibrated and used to measure water temperature, electrical conductivity (EC), and pH in the field. The EC meter was checked daily with a conductivity standard (KCl solution of 1413 and 12,880 µS/cm).

The pH was calibrated daily using three pH buffer standards (4.01, 7.00, and 10). Groundwater samples were analyzed for physiochemical major and minor ions, nutrients, and trace elements. TDS, TSS, and H_2S were analyzed in the laboratory of GEOSURV-Iraq. Ion Chromatography type IC, Metrohm-881-Compact were used to analyze anions (Cl^-, NO_3^{2-}, PO_4^{3-}, SO_4^{2-}) and cations (Na^+, Ca^{2+}, Mg^{2+}, and K^+). Bicarbonate HCO_3^- ion was analyzed using acid titration methods. DOC was determined using Elementary Analysis System GmbH LiquiTOC type. Trace element concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS) with a Thermo Scientific Element X-SERIES 2 ICP-MS. A series of various trace elements, including Br, Ba, B, Fe, Al, Pb, Zn, Mn, Li, Cr, V, Cu, Co, Ni, As, Se, Mo, Cd, U, and Sb were determined in the studied groundwater samples to assess the safety of water for drinking and other uses. According to Sundaram *et al.* (2009), the balance between cations and anions is within the acceptable error limits of ±5 %.

The total hardness (TH) in ppm was determined based on Eq.1 (Hem, 1985; Todd and Mays, 2005).

$$\text{TH (as CaCO3)} = 2.497\ [Ca^{2+}\ \text{ppm}] + 4.118\ [Mg^{2+}\ \text{ppm}] \ldots\ldots (\text{Eq. }1)$$

RESULT AND DISCUSSION

Tables 1, 2 and 3, and the site locations in Fig.1 show the analytical results of the groundwater. The groundwater temperature of the LZRB displays a wide variation between 14.8 ºC and 24 ºC with a mean value of 20 ºC (Table 1), which is attributed to the lithological difference between subbasins aquifers, well depths, and hydrological conditions. The pH of the groundwater samples of the LZRB ranges from 7.0 to 8.2 with a mean of 7.64 (Table 1). Hence, the pH value of the groundwater in the LZRB is neutral to slightly alkaline, which can be attributed to the presence of carbonate rocks and the slightly alkaline nature of the soil. The increase of the pH in agriculture dominated in the lower part of the basin may be due to the contribution from agricultural infiltration. All water samples were within the acceptable range for drinking. The DOC has a limited variation ranging from 0.33 ppm to 1.15 ppm (Table 1). The low concentrations of DOC may indicate limited impacts of land use as agricultural activity or limited decomposition of organic matter on groundwater DOC levels.

Table 1: Physiochemical parameters of groundwater during the wet season (April 2014)

S.ID	Sampling positions	Air T.	Water T.	DOC	H_2S	pH	EC	TDS	TH
Unit		C˚	C˚	ppm	ppm		µs/cm	ppm	ppm
GW1	38 N 512123, E 3954195	17.1	18.3	0.45	3.4	7.38	567	380	268
GW2	38 N 511462, E 3967541	20.4	14.8	0.6	4.1	7.77	616	402	170
GW3	38 N 503715, E 3991025	21.1	19.5	0.94	4.1	7.4	635	418	279
GW4	38 N 510297, E 4002395	18.2	18.4	0.43	3.4	7	531	350	243
GW5	38 N 477114, E 4005781	26.2	20.4	0.39	5.44	7.4	504	355	282
GW6	38 N 464761, E 3994763	26	18.5	0.69	3.4	7.8	421	283	237
GW7	38 N 461560, E 3972036	21.1	23.7	0.34	3.1	8.2	1069	706	72
GW10	38 N 451466, E 3992993	22.5	18.9	0.64	3.1	7.6	786	562	389
GW11	38 N 491004, E 3955852	25	21	0.83	4.1	7.3	897	685	439
GW12	38 N 400605, E 3951756	22.3	21	-	4.1	8.17	453	315	214
GW13	38 N 398516, E 3962705	26.5	20	-	2.7	8.2	621	432	205
GW14	38 N 416425, E 3946494	27.1	24	0.54	4.4	7.5	3450	2500	1563
GW15	38 N 414263, E 3966887	21	21.2	0.33	5.1	7.5	596	386	283
GW16	38 N 444645, E 3943811	29.5	18.5	0.44	5.1	7.8	386	255	189
GW17	38 N 422436, E 3957014	27.2	22.3	0.55	4.8	7.4	870	561	388
GW18	38 N 423033, E 3971733	21.2	23.3	-	3.4	8.07	419	259	198
GW19	38 N 446494, E 3968246	24.1	19.6	0.69	3.4	7.7	468	303	226
GW20	38 N 483946, E 3978070	17	21	0.39	2.7	7.6	565	385	275
Sp1	38 N 517263, E 3942650	18.8	18	0.99	7.8	7.5	393	255	193
Sp2	38 N 509502, E 3965503	22.6	16.8	1.15	6.8	7.5	381	261	212
Min		17	14.8	0.33	2.7	7	381	255	72
Max		29.5	24	1.15	7.8	8.2	3450	2500	1563
Mean		22.52	19.8	0.62	4.21	7.64	588	398	251
SD		3.6	2.33	0.24	1.33	0.33	667	489	305
Human Drinking IQS (2009)		-	-	-	-	6.5-8.5	-	1000	500
WHO (2011)		-	-	-	-	6.5-8.5	-	1000	500
Note: Gw14 is eliminated from the calculating mean, TH; Total hardness as CaCO3. GW: groundwater well sample, Sp: spring sample.									

The H_2S of groundwater is ranging from 2.7 to 7.8 ppm (Table 1). Sources of hydrogen sulfide in groundwater could have occurred from anthropogenic sources, such as leakage from wastewater disposal sites, or naturally by biochemical processes and inorganic reactions (Mukhopadhyay *et al.*, 2007). Thus, the presence of high H_2S may be derived mainly from sulfate-reducing bacteria acting on sulfate minerals of the geological formations. According to Soran (2008), the SO_4^{2-} concentration in the groundwater is mainly derived from gypsum dissolution and the presence of salt lenses, which characterize the Pliocene fluvial sediments within the area.

TDS in the groundwater of the LZRB ranges from 255 ppm in the spring sample (Sp1) to 2500 ppm in the well (GW14) with a mean of 398 ppm (Table 1). The groundwater salinity generally increases from the northeast toward the southwest along the groundwater flow path.

This can be attributed to the increase in the interaction time between water and sediments and rocks, and therefore, increases the dissolved ions in groundwater. Variations in the lithology of sub-basins aquifers, agricultures activity, dissolution of soil salts, and spills from wastewaters give reasons for the large difference in TDS value (Thivya *et al*., 2013). According to Hillel’s (2000) classification, for most of the sample’s area of freshwater class, four samples (GW7, GW10, GW11, and GW17) are slightly brackish, and only one sample GW14 is moderately saline. The EC of all groundwater samples is within the range of 381 µs/cm in the spring sample (Sp2) to 3450 µs/cm in the well (GW14) with a mean of 588 µs /cm (Table 1).

The spatial variation in the EC value of the groundwater samples is limited except for sample no. GW14. This well has recently been dug to a depth of 40 m within agricultural land and lies on slope sediments weathered from detritus geologic formations, which are characterized by high salty mineral content. Furthermore, there is a sewage source located near the well. Hence, the geogenic origin is expected to be the main responsible factor for the high EC value even though the anthropogenic factors cannot be ignored. The total hardness of the $CaCO_3$ in the groundwater samples of the LZRB ranged from 72 ppm to 1563 ppm with a mean of 250.6 ppm (Table 1). Most of the groundwater samples are of hard class according to Spellman's (2013) classification, and very hard class according to Bagley *et al*. (1997).

- **Hydrochemistry of major, minor, and nutrient ions**

Calcium ion has the highest value among the other cations in all groundwater and spring samples. It ranges from 13.1 ppm (GW7) to 384.6 ppm (GW14), with a mean of 67.9 ppm.

Mg^{2+} ranged from 6.33 ppm to 146.3 ppm with a mean of 19.7 ppm (Table 2). The spatial distribution of the Ca^{2+} and the Mg^{2+} showed that the maximum concentration of both cations is determined at sample GW14 (Fig.4A and B, and Table 2).

The highest concentration of the Ca^{2+} is noticed around Dokan Lake within the zone dominant by exposure of carbonate rocks and the in the lower part of the LZRB (Fig.4A). The concentrations of Na^+ and K^+ range from 1.72 ppm to 227.8 ppm, and from 0.39 ppm to 2.97 ppm, respectively. The mean concentrations of the Na^+ and the K^+ are 30.9 ppm and 1.11 ppm, respectively (Table 2).

According to Al-Saady *et al*. (2015), the highest value of the Na^+ is recorded in GW7 nearby Taq-Taq City, which lies within the mixed barren land class and geologically within the clastic of the Mukdadiyah Formation. The highest K^+ content is recorded in the samples GW7 (2.96 ppm) and GW14 (2.97) (Fig.4A and Table 2). Like Na^+, weathering of rocks is the main source of K^+ in water (Murhekar and Rathod, 2011), even though the effect of agriculture and other anthropogenic activities cannot be ignored. Among the anions, the HCO_3^- is the most prevalent ion in the groundwater. The concentrations of HCO_3^- in the groundwater samples vary from 199.9 to 492.4 ppm with a mean of 285.56 ppm (Table 2).

The highest concentration is recorded in GW10 (Table 2). This sample lies within cropland and pasture class and geologically within the Mukdadiyah Formation. HCO_3^- concentrations, generally, have shown high values in the studied groundwater samples. Weathering of the carbonate rocks and/ or alumino-silicate minerals are the main source of HCO_3^- in the groundwater. Thus, the dissolution of the dominant carbonate rocks in the LZRB is the main source of the HCO_3^- ion. Fig.4B shows the spatial distribution of the HCO_3^- ion, where there is a general decrease in the lower part of the basin.

The concentrations of the chloride (Cl^-) range from 2.5 to 113.2 ppm with a mean value of 13.45 ppm (Table 2). The maximum Cl^- concentration is recorded at GW14 and GW7 (Table 2).

Table 2: Major nutrient ions and minor elements of groundwater samples (in ppm), during the wet season in April 2014 maximum contaminant level (MCL) of drinking water standards (WHO, 2011)

S.ID	**Ca^{2+}**	**Mg^{2+}**	**Na^+**	**K^+**	**HCO_3^-**	**SO_4^{2-}**	**Cl^-**	**Si**	**Sr**	**NO_3^-**	**NH_4^+**	**PO_4^{3-}**
GW1	75.04	19.6	4.57	0.97	289.9	11.6	19.37	6.71	0.29	58.06	<0.05	0.04
GW2	45.24	13.9	84.78	1.37	349.3	33.47	10.33	7.68	1	40.52	<0.05	0.04
GW3	80.37	19	7.54	2.12	285.3	73.18	12.8	7.16	1.16	43.18	<0.05	0.06
GW4	70.55	16.3	10.29	0.76	323.4	14.95	5.71	10.51	0.6	32.4	<0.05	0.04
GW5	83.4	17.8	5.61	0.82	299.9	42.48	4.82	5.13	0.51	11.13	<0.05	0.03
GW6	71.74	14	10.12	0.39	301.7	25.44	4.97	4.36	0.72	19.22		0.02
GW7	13.12	9.6	227.8	2.96	275.4	225.3	79.94	7.51	1.65	4.21	<0.05	0.03
GW10	81.91	44.7	33.9	0.5	492.4	38.22	15.45	8.25	2.56	41.55	<0.05	0.04
GW11	113.3	37.9	11.08	1.59	369.4	172.2	17.83	10.98	1.99	41.04	<0.05	0.08
GW12	59.22	15.9	13.35	2.28	199.9	57.59	11.14	3.28	0.68	10.19	<0.05	0.02
GW13	54.51	16.8	74.06	0.78	248.6	122.4	4.97	6.73	1.53	15.5		0.03
GW14	384.6	146.3	211.9	2.97	202.2	1710	113.2	5.3	4.39	68.01	<0.15	0.03
GW15	67.22	27.9	28.89	0.63	341.6	44.06	5.06	9.17	1.58	23.02	<0.05	0.04
GW16	49.54	15.9	12.93	0.85	216.9	22.16	7.58	6.45	0.87	9.92	<0.05	0.02
GW17	107.3	29.1	26.72	1.13	274.3	168.7	24.22	8.95	3.01	64.65	<0.05	0.05
GW18	51.71	16.8	11.41	1.05	204.7	38.61	7.7	5.69	0.82	43.5	<0.15	0.02
GW19	63.23	16.6	8.94	1.2	221.6	38.64	7.78	5.32	0.92	20.92	<0.05	0.04
GW20	69.62	24.5	11.61	0.56	270.5	48.15	9.2	7.62	0.98	48.16	<0.05	0.04
Sp1	67	6.3	2.24	0.5	229.2	12.4	4.13	5.36	0.24	20.66	<0.05	0.04
Sp2	65.71	11.5	1.72	0.55	231.6	26.68	2.5	2.7	0.19	4.1	<0.05	0.02
Min.	13.12	6.3	1.72	0.39	199.9	11.6	2.5	2.7	0.19	4.1	0.05	0.02
Max.	384.6	146.3	227.8	2.97	492.4	1710	113.2	10.98	4.39	68.01	0.15	0.08
Mean	67.88	19.7	30.92	1.11	285.7	64.01	13.45	6.74	1.28	29.05		0.04
SD	73.97	29.8	65.43	0.79	71.1	372.93	27.85	2.19	1.04	19.87		0.01
(MCL) of drinking water standards **IQS (2009)**	150	100	200	-	-	400	350	-		50	-	-
WHO (2011)	100	125	200	12	-	250	250	-		50	-	-
Note: Gw14 is eliminated from calculating the mean												

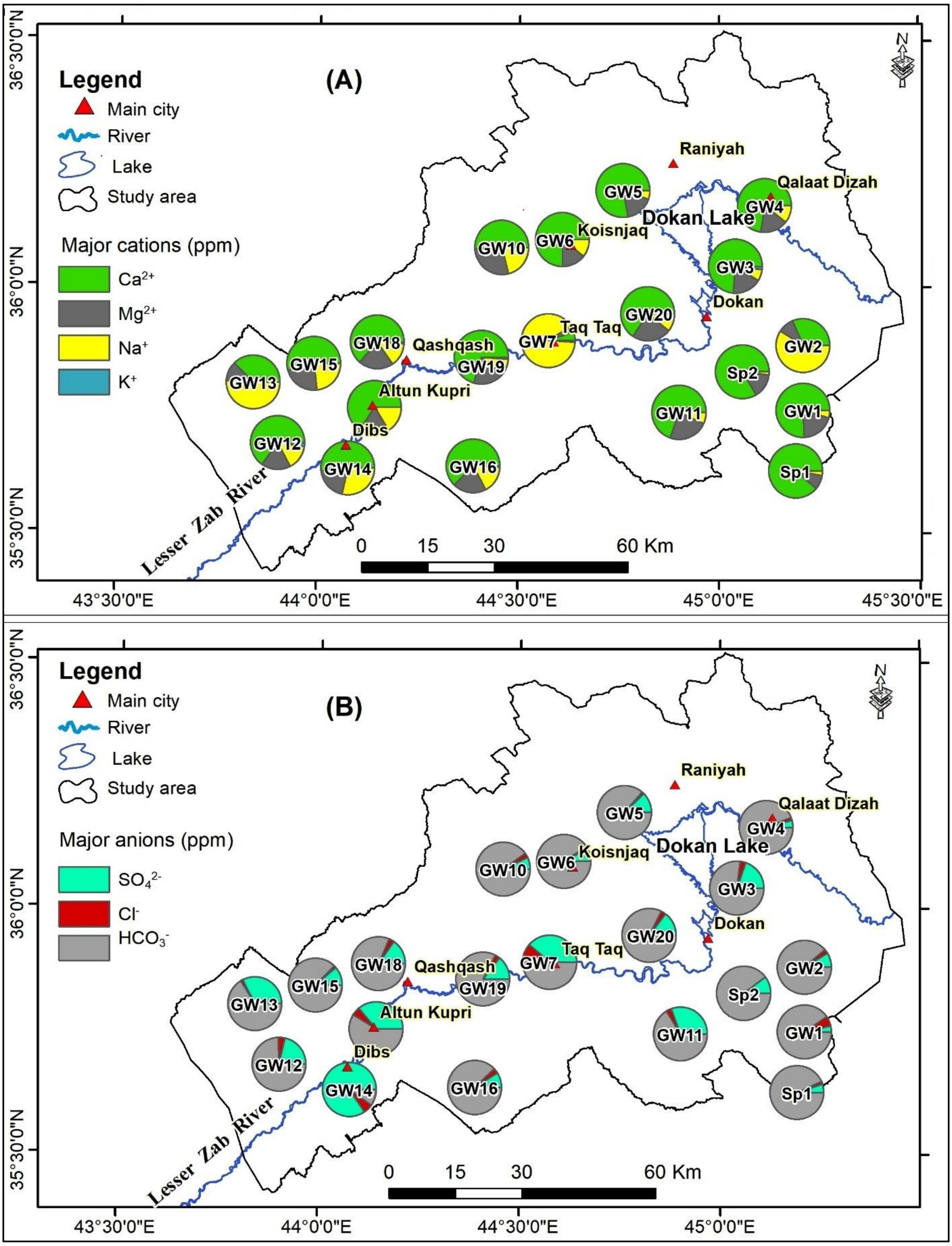

Fig.4A and B: Pie chart maps of the major ions in the groundwater samples during the wet season

Cl^- inter the environment from natural and anthropogenic sources, such as soils, geologic deposits, landfills, and industrial and agricultural practices (Appelo and Postma, 2005; Panno *et al*., 2006; Mullaney *et al*., 2009; Singh *et al*., 2014). The presence of Cl^- ion in the studied samples can be mainly attributed to the natural sources and agricultural activities, such as irrigation water before reaching the groundwater.

Weathering of the evaporite minerals, particularly, halite can be considered the main source of chloride in the groundwater (Singh *et al*., 2014). The content of the SO_4^{2-} in the analyzed groundwater samples shows that the concentrations vary from 11.6 ppm (GW20) to 1710 ppm in the GW14 with a mean of 64.01 ppm (Table 2). High concentrations of the SO_4^{2-} are recorded at GW14 and GW7 (Table 2). The spatial distribution of the SO_4^{2-} shows increases towards the lower part of the main basin (Fig.4B). The highest sulfate concentration in the groundwater of the lower part attributes mainly to the lithogenic origin, whereas the gypsum beds exist in these areas as a part of the lithological sequence of the Fatha Formation.

NO_3^- is the prevalent nutrient detected in the studied samples. The concentrations of NO_3^- are varying from 4.1 ppm to 68.01 ppm with a mean of 29.05 ppm (Table 2). High concentrations are recorded in wells GW1, GW14, and GW17 with a concentration of 58.06, 68.01, and 64.65 ppm, respectively (Table 2). Land use and associated activities could be the governing factor in the distribution of nitrate in unconfined aquifers of the LZRB. NH_4^+ and PO_4^{3-} have very low concentrations in all groundwater samples. Anthropogenic sources of nitrogen and phosphorus in water wells attribute mainly to inorganic fertilizer and the discharge of wastewater from the urban area. Groundwater samples of the considered aquifers of the LZRB contain an appreciable level of dissolved silica. The concentrations of Si range from 2.7 to 10.98 ppm with a mean of 6.74 ppm (Table 2). The highest concentrations were recorded in the samples GW4 (10.51 ppm) and GW11 (10.98 ppm), which are located within the agricultural land and the urban and built-up land, respectively. The concentration of silica in the groundwater implies that silica is one of the major chemical components of the water samples from the studied wells. A high concentration of dissolved silica attributes mainly to weathering the high silica content of parent rocks. The strontium concentrations in the studied samples range from 0.19 ppm to 4.39 ppm with a mean of 1.28 ppm (Table 2). The groundwater samples of the LZRB display a large variation in Sr values. Generally, the concentrations of Sr in almost all fresh waters range between 0.5 and 1.5 ppm (ATSDR, 2004), whereas its concentration in seawater is about 8 ppm (Hem, 1985). It can be derived from the digenetic transformation of aragonite to calcite in the carbonate rocks, and it can be released into groundwater as those minerals dissolve.

- **Hydrochemistry of the trace elements**

Trace elements content in the groundwater are controlled by many geochemical processes, such as precipitation-dissolution, biota, and land use (Leung and Jiao, 2006; Rifat *et al*., 2016; Mason, 2013; Thuyet *et al*., 2016; Mora *et al*., 2017). Although some trace elements are essential to humans, the high concentration of these elements can be carcinogenic and toxic. Identifying the distribution of trace elements in water is an urgent issue to identify contamination mechanisms and develop suitable monitoring programs (Sappa *et al*., 2014). The concentrations of the trace elements are summarized in Table 3 and the results were compared with the drinking-water quality guidelines of WHO (2011) and IQS (2009). **Bromide (Br)** is a trace element present naturally with a low level in the groundwater (Magazinovic *et al*., 2004). Groundwaters were characterized by higher bromide concentrations, while surface waters were characterized by lower concentrations (Good and VanBriesen 2019). Therefore, it can be used as an indicator of the discharge of groundwater to surface water in the LZRB. Bromide concentrations in water from wells of the unconfined aquifer range from 19.98 ppb to 252.3 ppb with a mean of 71.6 ppb (Table 3), which is within the world mean, from trace amounts to about 500 ppb (WHO, 2017). Water samples collected from three wells GW14, GW7 and GW10 contained elevated bromide concentrations of 252.3 ppb, 209.2 ppb, and 104.2 ppb, respectively. The concentration of **Barium (Ba)** in the groundwater is controlled by the solubility of barite, therefore, high concentrations of the

SO_4^{2-}, govern Ba^{2+} concentration due to saturation with barite (Giménez-Forcada and Vega-Alegre, 2015). Concentrations of Ba in drinking water are, generally, below 100 ppb, although concentrations above 1000 ppb have been measured in drinking water derived from groundwater (WHO, 2017). The concentration of the Ba in the groundwater samples is varying from 11.5 ppb to 412.7 ppb with a mean of 89.6 ppb (Table 3). In general, the concentrations of Ba in the studied samples are less than 173 ppb, except for the sample from groundwater well Gw10, which has a value of 412.7 ppb and also records a high value of Zn. The primary source of barium in the groundwater results from the leaching and eroding of the sedimentary rocks into groundwater (Kojola *et al*., 1979). In most groundwater, **Boron (B)** is present naturally at concentrations of less than a few hundred ppb (Ravenscroft and McArthur, 2004). The high concentrations of B can be toxic to the plant causing disorder and growing limitations, especially, on soils of arid and semi-arid environments (Koç, 2007). For some plants, such as citrus, the toxic concentration of B is as low as 1000 ppb (Hem, 1985; Williamson and Carter 2001). Despite the lack of information regarding the effects of the B on livestock via watering, it is recommended that B in livestock water should not exceed 5000 ppb (EPA, 1988; CCME 1999). Also, human exposure to large amounts of B can affect the stomach, intestines, liver, kidney, and brain (ATSDR, 2010). Thus, the WHO designated a provisional guideline value of 500 ppb for drinking water (WHO, 2009). In the studied samples, the B content of groundwater samples ranged from 11.79 ppb to 316.2 ppb with a mean value of 81 ppb (Table 3). The highest concentrations of B with values of 316.2 ppb and 247.9 ppb were recorded at Gw13 and GW7, respectively. The evaporite dissolution (Butterwick *et al*., 1989) and clay minerals weathering (Goldberg *et al*., 1996a; Weiner, 2010) consider the main source in certain areas and also wastewater discharges (WHO, 2009).

Aluminum (Al) concentrations ranged from 8.51 ppb to 45.13 ppb with a mean of 25.95 ppb (Table 3). The highest values of Al concentrations are 68.4 ppb and 67 ppb, which are recorded at GW12 and GW13, respectively. Al concentration in most natural waters is extremely low as a result of the low mobility of this element in the structure of aluminosilicate minerals (Filipek *et al*., 1987). However, the presence of Al concentrations between 100 ppb and 200 ppb often leads to consumer complaints as a result of the deposition of aluminum hydroxide floc and the exacerbation of discoloration of water by iron (WHO, 2017). There is a general increase of Al content towards the lower part of the main basin attributed, mainly to the dominance of clay sediment compared to the carbonate rock in the middle part. None of the water samples contained aluminum above the specified maximum contaminant level.

The **Iron (Fe)** concentrations in the studied samples range from 18.1 ppb to 106 ppb (Table 3). Maximum Fe concentration in groundwater was observed in GW13, which lies within cropland and pasture area, and geologically, within polygenetic sediments. The most common natural source of Fe in the groundwater is weathering iron minerals. Like Al, the concentration of Fe shows a general increase from the northwest to the southeast. The general increase in the Fe content may be attributed to a change in the lithology of the main basin from carbonate dominant nearby and the north of Dokan Lake to detritus dominant to the south of the Lake. Consequently, the occurrence of the iron may rather be related to the lithological type and source rocks of the sediments that constitute the aquifers. The aquifers are predominantly detritus sediment with brown color due to the iron oxide coatings and stains in the lower part of the basin. The high concentration of Fe in some wells could be attributed to the interaction between organic matter and Fe minerals, whereas Fe(II)-organic-matter complexes are dominant in the environment and represent a significant factor controlling the behavior of the Fe and pollutants (Mondal *et al*., 2010; Peng *et al*., 2018).

Agriculture land, sewage, and landfill leachate may also contribute Fe to groundwater in the local area.

Table 3: Trace elements of groundwater samples during the wet season in April 2014 (ppb), maximum contaminant level (MCL) of drinking water standards (WHO, 2011; IQS, 2009) and water for irrigation (CCME 1999; EPA, 2012)
N.S: no standard guide value available

Sample ID.		Br	Ba	B	Fe	Al	Pb	Zn	Mn	Li	Cr	V	Cu	Co	Ni	As	Se	Mo	Cd	U	Sb
GW1		48.07	56.27	16.96	33.24	22.45	10.83	7.48	1.82	3.91	3.43	2.74	0.90	0.063	0.36	0.22	0.24	0.7	0.008	0.54	1.34
GW2		51.71	45.46	193.9	46.75	15.89	45.13	245.2	2.07	15.69	3.57	1.8	302.4	0.098	1.88	1.97	1.47	1.6	0.042	0.5	2.15
GW3		65.6	71.72	28.22	38.16	24.75	14.42	74.19	6.55	6.75	3.65	2.22	2.23	0.069	0.52	0.42	0.74	3.9	0.013	0.88	1.62
GW4		59.34	40.38	32.31	18.1	8.51	9.14	5.74	1.12	3.3	2.02	2.37	0.58	0.039	0.27	0.23	0.19	0.73	0.005	0.98	1.5
GW5		36.98	34.6	34.94	22.65	11.17	13.95	169.4	1.32	10.04	3.88	1.86	0.66	0.046	0.22	0.22	0.4	2.87	0.018	0.65	1.71
GW6		42.52	90.53	15.5	23.86	13.21	14.4	23.42	1.34	2.17	3.16	2.65	0.39	0.069	0.48	0.29	0.54	2.02	0.004	0.47	1.59
GW7		209.2	24.48	247.9	47.59	29.36	11.43	8.12	4.96	29.45	2.53	214.8	0.98	0.053	0.29	1.37	7.3	5.06	0.008	4.11	1.35
GW10		104.2	412.7	80.29	45.68	24.66	10.62	633.3	1.94	20.14	3.50	5.62	2.16	0.062	0.49	0.37	0.4	2.84	0.059	4.89	1.89
GW11		72.82	43.57	59.34	39.18	18.78	10.19	34.52	2.34	11.52	3.98	3.8	1.61	0.07	0.7	0.36	1.65	2.37	0.007	1.29	1.12
GW12		70.71	67.1	44.57	27.82	68.41	13.62	6.73	2.55	4.06	2.76	3.47	0.8	0.067	0.71	0.76	0.31	1.52	0.005	0.78	1.4
GW13		37.16	44.23	316.2	106	67.05	15.1	111.8	20.79	12.75	13.92	8.52	3.34	0.154	0.97	0.44	0.2	6.09	0.023	3.40	1.58
GW14		252.3	11.5	304.7	27.72	11.64	5.74	8.54	1.19	18.08	3.49	1.96	0.27	0.032	0.29	0.19	0.94	2.43	0.004	3.51	0.71
GW15		47.73	102.5	131	42.6	21.72	13.56	111.6	2.12	13.54	11.85	11.58	0.86	0.047	0.36	0.44	0.4	1.73	0.01	2.68	1.46
GW16		39.09	99.15	50.64	26.86	15.15	9.85	60	1.43	5.72	1.98	5.91	0.68	0.062	0.18	0.42	0.12	3.26	0.008	1.41	1.56
GW17		88.39	84.22	116.8	86.65	38.71	11.64	27.2	2.29	12.01	3.98	4.08	1.36	0.101	0.72	0.48	0.35	2.97	0.011	4.51	1.55
GW18		40.44	115.3	53.17	70.66	38.65	15.4	80.97	2.42	8.23	4.17	5.11	1.1	0.064	0.37	0.38	0.18	2.50	0.01	1.35	1.16
GW19		50.14	173.7	52.39	38.06	20.54	19.85	10.5	1.93	5.03	3.78	2.02	0.67	0.072	0.49	0.5	0.37	1.92	0.007	1.12	2.14
GW20		65.76	220.6	41.17	36.94	19.42	11.01	25.94	1.82	4.54	3.58	3.96	1.06	0.068	0.22	0.56	0.21	1.32	0.004	0.63	1.48
Sp1		29.56	31.48	11.79	35.91	25.24	12.36	4.93	1.74	2.31	3.59	2.47	0.42	0.086	0.57	0.2	0.23	0.73	0.004	0.43	1.57
Sp2		19.98	22.8	11.88	32.56	23.78	9.39	5.43	1.71	1.63	1.92	0.75	2.35	0.065	0.4	0.12	0.31	0.72	0.029	0.36	1.31
Min		19.98	11.5	11.79	18.1	8.51	5.74	4.93	1.12	1.63	1.92	0.75	0.27	0.03	0.18	0.12	0.12	0.7	0.004	0.36	0.71
Max		252.3	412.7	316.2	106	68.41	45.13	633.3	20.79	29.45	13.92	214.8	302.4	0.15	1.88	1.97	7.3	6.09	0.06	4.89	2.15
Mean		71.59	89.61	92.18	42.35	25.95	13.88	82.75	3.17	9.54	4.24	14.38	16.24	0.07	0.52	0.5	0.83	2.36	0.01	1.72	1.51
SD		58.41	92.13	96.89	21.95	16.38	7.94	144.58	4.34	7.24	3.05	47.24	67.36	0.03	0.38	0.44	1.58	1.44	0.01	1.52	0.33
(MCL) of drinking water standards	**IQS (2009)**	N.S	700	500	300	100	10	3000	100	N.S	50	N.S	1000	N.S	20	10	N.S	N.S	3	N.S	N.S
	WHO (2011)	N.S	700	2400	300	200	10	3000	500	700	50	N.S	2000	N.S	70	10	40	70	3	30	20
Water for irrigation	**CCME 1999; EPA 2012**	N.S	N.S	750	5000	5000	N.S	2000	200	2500	100	N.S	200	50	200	100	N.S	10	10	N.S	N.S

Lead (Pb) is a bio-accumulative and highly toxic element that can cause irreversible damage to body organs, such as kidneys and the nervous and reproductive systems (Pazand *et al.*, 2018). Concentrations of Pb in drinking water are, generally, below 5 ppb. Pb was determined in all groundwater samples ranging from 5.7 ppb to 45.1 ppb with a mean of 13.88 ppb (Table 3). The highest value of Pb was obtained from well GW2, which lies within the urban and built-up areas. This may indicate the contribution of anthropogenic sources of the Pb in the studied aquifer.

Normally, the concentration of **Zinc (Zn)** in the groundwater does not exceed 10 ppb (ATSDR, 2011). Although the WHO has not set a guideline value for drinking water (WHO, 2008), a high concentration of zinc may affect the acceptability of drinking water. Zn concentrations range from 4.93 ppb to 633.3 ppb with a mean of 82.8 ppb (Table 3). The elevated concentration of Zn with a value of 245.2 ppb in groundwater samples GW2, which lies within the urban and built-up areas of Humara Qaum village, this sample also characterized by high values of Cu and Pb. GW10 with a Zn value of 633.3 ppb, which is located within the agricultural land area of the wheat crop, therefore, the use of fertilizer may be the probable source of the Cu, which also has a high value of Ba.

Levels of **Manganese (Mn)** in fresh water, typically, range from 1 ppb to 200 ppb (WHO, 2021). Mn and Fe closely occur in water, and Mn concentration is mostly lower than Fe (El Araby *et al*., 2009; Homoncik *et al*., 2010). pH and redox conditions consider the primary controlling factors on the concentration of Mn in water where the solubility of the Mn increase under anaerobic and acidic conditions (Nádaská *et al*., 2010). The measured concentrations of Mn in the unconfined aquifer of the LZRB range from 1.2 ppb to 20.8 ppb with a mean of 3.17 ppb (Table 3). Mn concentrations in the studied groundwater show a limited variation and the highest concentration was recorded at GW13 in the lower western reach of the basin.

The WHO has no published limits on **Lithium (Li)** in drinking water (WHO, 2017), whereas the Eurasian Economic Union designated a provisional guideline value of 30 ppb for drinking water (Lindsey *et al*., 2021). In the studied samples, Li concentrations vary from 1.6 ppb to 29.5 ppb with a mean of 9 ppb (Table 3). Li concentrations were, generally, low in the studied samples and, relatively, high values of the Li were recorded in two wells GW7 (29.5 ppb) and GW10 (20.1 ppb) where both of them have, relatively, high EC values.

Even though **Vanadium (V)** is one of the widely distributed trace elements in the earth’s crust, there are few studies on the significant sources and behavior of V in water (Wright and Belitz, 2010; Imtiaz *et al*., 2015, Alkinani and Merkel, 2017). The concentration of V in natural water is generally, less than 1 ppb (Oroz *et al*., 2014; Wright and Belitz, 2010). The natural release of the V to water and soils occurs primarily as a result of weathering of rocks and soil erosion (WHO, 2011; ATSDR, 2012). The most important anthropogenic sources of V include the combustion of fossil fuels, particularly, residual fuel oils, which constitute the single largest overall release of V to the atmosphere (ATSDR, 2012). V pentoxide exposure (acute and chronic) in both experimental animal and human studies indicates a systemic pathophysiological and pathological influence on cell metabolism and tissue function (Cooper, 2007). The International Agency for Research on Cancer (IARC) has determined that V is possibly carcinogenic to humans (ATSDR, 2012), due to the generally low concentrations, water intake is not considered among the major sources of V in the human body (Oroz *et al*., 2014). However, some national regulations set a limit for V in drinking water, such as in Serbia (1 ppb), California (50 ppb), and the Czech Republic and Ukraine (100 ppb) (Oroz *et al*., 2014; Wright and Belitz, 2010). In addition, the recommended MCL for V in irrigation and livestock watering is 100 ppb (EPA, 1988; CCME 1999; EPA, 2012). The V concentrations in the groundwater of the LZRB are ranging from 0.75 ppb to 214.8 ppb (Table 3). The abnormal value of 214.8 ppb of the V was recorded in well GW7, which was drilled near the fuel-guzzling electrical generator under very poor environmental conditions. Hence, the elevation of the V in this well can be attributed to oil contamination.

In groundwater, **Uranium (U)** concentration is, generally, low with a range of 0.1 – 1 ppb (Smedley *et al*., 2006). Because of the increased awareness of the health hazards of the U, there has been growing pressure to tighten drinking water standards for the U in recent years (Fairlie, 2009). In the studied samples, U concentrations in groundwater are ranging from 0.36 ppb to 4.89 ppb with a mean of 1.63 ppb (Table 3). The maximum U content was observed in well GW10. According to the World Health Organization (WHO, 2011), the concentration of U in drinking water should not exceed 30 ppb. However, some countries have placed even stricter limits on the allowed U in drinking water; the limit of U in drinking water in Germany is 10 ppb (Trinkw, 2011). Human activity also has a potential effect on the U concentration as using of phosphate fertilizers on agricultural land. The relatively increased concentration of U in the lower part of the basin could be attributed to the increase in agricultural activity in this part, where the U is associated with phosphatic fertilizers.

- **Classification and hydrogeochemical facies of groundwater**

Classification of water is used for basic characterization of the chemical composition to differentiate chemical types of water and help identify the dominant types. The changes in hydrogeochemical facies and water types of groundwater in the LZRB can be interpreted by various hydrochemical methods. The hydrochemical classification of water can be identified by using the Kurlolov formula (Ivanov *et al*., 1968), Piper trilinear diagram, or any other methods. According to Piper's (1944) classification, all samples are classified as Ca^{2+}-HCO_3^- water type except for samples GW2 and GW13, which are categorized as Na^+- HCO_3^- and sample GW7, which is classified as Na^+-SO_4^{2-} (Fig.5). This is probably caused mainly by the dissolution of sodium chloride and gypsum in the Fatha Formation, particularly, in the lower part of the LZRB.

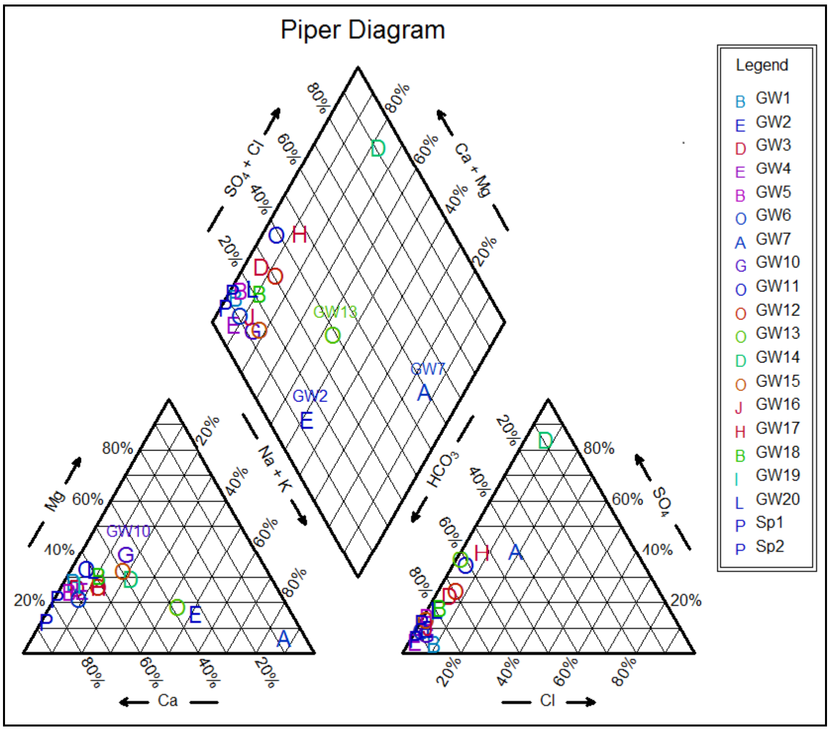

Fig.5: Piper diagram of the groundwater samples of the LZRB during the wet season

- **Mechanisms controlling groundwater chemistry**

Reactions between the groundwater and the aquifer minerals have a direct effect on water chemistry, and also contribute in understand the groundwater genesis (Cederstrom, 1946). Gibbs diagram is widely used to assess the governing processes controlling dissolved chemical constituents, such as atmospheric precipitation, rock dominance, and the evaporation crystallization process. These three mechanisms are the major controlling processes on the chemistry of the TDS of the world's waters (Gibbs, 1970). Where the Na^+ and Ca^{2+} concentrations are expressed in milliequivalents per liter and total dissolved solids in milligrams per liter. According to Gibbs’s (1970) diagram, the ratios of dominant anions and cations are displayed on X-axis and the variation in TDS on Y-axis. Gibbs diagrams, representing the ratio for cations $[Na^+/ (Na^++Ca^{2+})]$ and $[Cl^-/ (Cl^-+ HCO3^-)]$ as a function of TDS (Fig.6). Gibbs’s diagram shows that the rock-water interaction represents the main factor affecting the groundwater chemistry of the LZRB and can be attributed to the dissolution of the evaporate rocks, particularly, in the Fatha Formation. Three samples are shifted from other groundwater samples because they are richer in Na^+. Groundwater chemistry is, generally, controlled by weathering of minerals, precipitation of secondary minerals, and ion exchange.

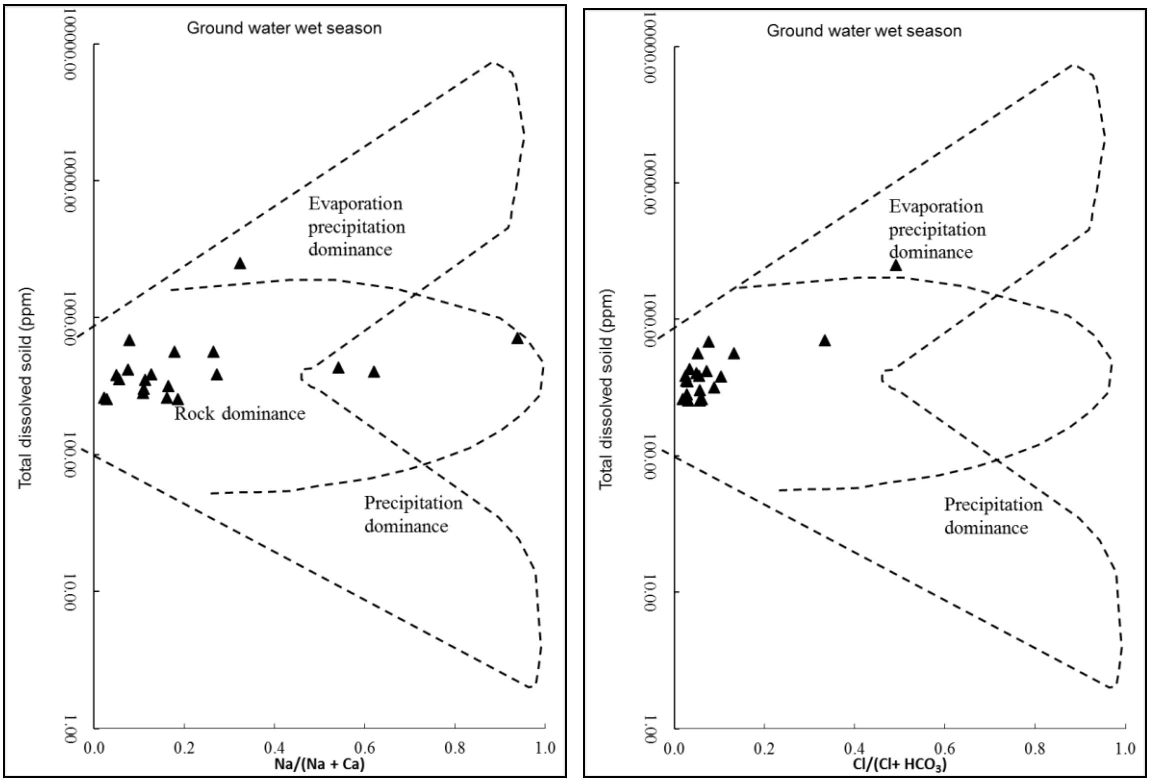

Fig.6: Gibbs diagrams show the mechanism controlling the groundwater chemistry of the LZRB

- **Suitability of water for different uses**

The evolution of water suitability for drinking, industrial, and agricultural uses is determined depending on the criteria for that use. Drinking water standards of (ATSDR, 2011) and Iraq (IQS, 2009) were used as a basis to assess the appropriateness of water for drinking use. All groundwater samples during the wet season are suitable for drinking, according to recommended limits, except for the Pb, which exceeds the standard limit for most samples. There are one groundwater sample, GW14, which has TDS, Ca^{2+}, SO_4^{2-} and

NO_3^- higher than the recommended limit, and two samples, GW1 and GW17, that exceed the recommended limit for NO_3^-.

The suitability of water for livestock, usually, takes into account type, daily water amount, and effect of specific substances on the different species.

All groundwater samples of the high flow season are within the excellent type, except for sample GW14, which lies within very satisfactory (Ayers and Westcot, 1985; EPA, 1988).

Evaluation of irrigation water quality is necessary for the planning, and design of irrigation systems to be certain that no harmful salts or constituents are present (Sangodoyin and Ogedengbe, 1991). There are many standards suggested to assess irrigation water quality as a salinity hazard and sodium hazard. Classification of the studied groundwater samples based on salinity hazard as measured by EC shows that most samples are within the good class and only three samples (i.e., GW7, GW11, and GW17) are within the permissible class according to Bauder *et al*. (2011) classification. All groundwater samples from the wet season lie within the low hazard class according to sodium hazard based on SAR values (Bauder *et al*., 2011).

The salinity diagram of Richards (1954) is used to assess the quality of irrigation water based on the EC and SAR values (Fig.7). Groundwater samples lie mainly within the C2-SI class, except for five samples that are GW7 (which is plotted within the C3-S2 class) GW10, GW11, and GW17 (which are plotted within the C3-SI class), and GW14 (which is plotted within the C4-SI class).

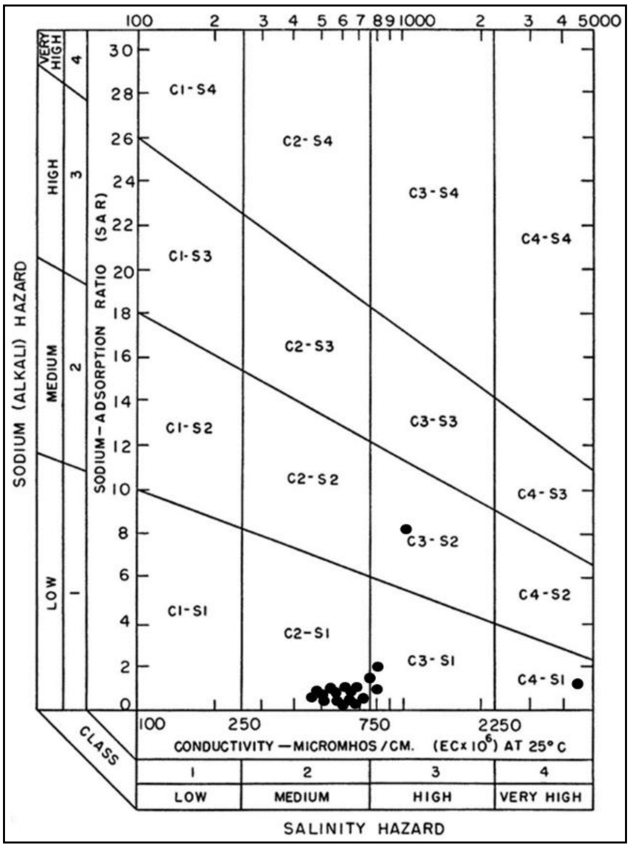

Fig.7: Classification of the groundwater irrigation using salinity diagram

CONCLUSION

The groundwater of the LZRB is neutral to slightly alkaline in nature and HCO_3^-, SO_4^{2-}, Ca^{2+}, and Mg^{2+} are the major contributing ions to the dissolved solids, and NO_3^- is the major nutrients. Alkaline earth elements (Ca^{2+} and Mg^{2+}) exceed alkalis (Na^+ and K^+). For most groundwater sampling sites, total hardness is generally within the hard and very hard classes. The hydrogeochemical interpretation suggests that weathering of rock along with contributions from agricultural and other anthropogenic activities governs the groundwater composition of the LZRB. Ca^{2+}-HCO_3^- are the dominant hydrogeochemical facies in the groundwater of the basin. A high concentration of Ca^{2+} in the groundwater of the study area is due to the release of Ca^{2+} from aquifer materials.

A comparison of groundwater parameters with specified limits for drinking water shows that all groundwater samples, except well GW14, which exceeds the permissible limit of TDS, and two samples, GW1 and GW17, exceed the permissible limit for NO_3^- during the wet season are suitable for drinking, except for Pb, where it exceeds the standard limit for most samples. The presence of nitrate in all wells may be due to excessive application of nitrogen fertilizers or decay of plants and animals residue or disposal of domestic wastewater or sewage as well as infiltration from a septic tank. Sewage, increased use of pesticides, as well as different kinds of other contaminants have been released from urban lands, which contained lots of trace elements, representing non-point source pollution from urban and agricultural areas of the basin.

The groundwater of the studied samples is suitable for livestock drinking and irrigation. The results of the study showed that the distribution of minor and trace elements in groundwater wells of the LZRB exhibits noticeable spatial variation. Pb was identified as the main pollutant of concern among the studied trace elements. The highest accumulation for Pb with maximum concentration in sampling sites of GW2. Pb shows a strong correlation with Cu and Ni elements and can be used as a reliable urban tracer. The major sources of trace elements contaminating in groundwater of the LZRB may come from both natural and anthropogenic inputs, such as parent rocks, residue wastes from industrial, residential wastewater, and agriculture.

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