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Investigation the Origins of Groundwater Salinity in Baghdad City by Using Environmental Isotopes and Hydrochemical Techniques

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Abstract

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The hydrochemical and isotopic techniques have become one of the most popular and successful methods for determining the hydrogeochemical features of groundwater in recent years. A total of 15 samples were collected during wet (March, 2021) and dry (August, 2021) seasons. An approach with major elements (Cl⁻, Na⁺, Mg²⁺, Ca²⁺, and SO₄ ²⁻) and multi-isotope (²H, ¹⁸O) are used in this study to solve the geochemical variation of salinity in groundwater in Baghdad. The results of the analysis of groundwater samples in the study area showed that the major cations were Ca²⁺ and Na⁺, while the major anion was SO₄, Cl, and HCO₃. The Ca-SO₄ and Ca-Na-Cl-SO₄. hydrochemical facies are the dominant hydrochemical facies of groundwater on the Al-Karakh and Al-Russafa sides, respectively. Ca-HCO₃ was found to be the dominant hydrochemical facies of the Tigris River. Human activities and geochemical processes may have caused differences in hydrochemical Facies. According to isotope analysis, the study area has multiple sources of salinity. This can be attributed to the effects of natural dissolution of the salt compounds, mixing with sewage, and industrial water sink. The results and data from this work can be used to research groundwater recharge and interaction, as well as to protect groundwater quality.

Keywords: Groundwater; Salinity; Isotopes; Baghdad city

1. Introduction

Groundwater is a critical source of life and sustainability in arid and semi-arid regions. It is one of the most valuable natural resources in the majority of countries. As the world's population grows, so does the demand for groundwater to support urbanization, industrialization, and agriculture (Su and Wang, 2013). Salinization is major environmental adversity that affects soil and water resources, agriculture, and natural ecosystems. Salinity is a global issue, but it is especially severe in water-stressed arid and semi-arid regions where groundwater is the primary source of water. Increasing groundwater demand causes water table depletion and salinity to rise (Gopal, 2019). High levels of various elements, including sodium, sulfate, boron, fluoride, selenium, arsenic, and radioactivity, have also been linked to increased groundwater salinity (Rusi, 2018). Salinity is commonly expressed as Total Dissolved Solids (TDS) grams of salts per liter, but other proxies such as electrical conductivity (EC-S/cm) or chloride content (mg Cl per liter) are widely used. EC and chloride content can be converted to TDS by multiplying by 0.7 and 1.8, respectively (IAEA, 2004). Iraq is no exception in this regard, particularly in

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the southern parts, where groundwater demand has increased in recent decades. One of the most common and effective methods for determining the hydrogeochemical characteristics of groundwater are the hydrochemical and isotopic methods. have become essential components of the study of groundwater hydrogeochemical characteristics (Ako et al., 2012, Li et al., 2014; Bozdag, 2016). The oxygen and deuterium isotopes (¹⁸O and D) have preservative properties and are only affected by atmospheric conditions during recharging (Gat, 1996). In recent years, a large number of studies on the use of water isotopes in hydrological processes and the origin of salinity in groundwater have been published (Al-Paruany 2013; Ajeena, 2014; Ali et al; Nada, 2020). An approach with major elements (Cl⁻, Na⁺, Mg²⁺, Ca²⁺, and SO₄ ²⁼) and multi-isotope (²H, ¹⁸O) is used in this study to solve geochemical variation of salinity in groundwater in Baghdad.

2. The study Area

The study area is in Baghdad's central business district (Both side Al-Karkh and Russafa) (Fig. 1). The overall area is 1020 km². The research area is located between latitudes 33 10-33 29N and longitude 44 09-44 33 E. Climate data were gathered from meteorological stations in Baghdad. Annual rainfall ranges from 0.04 to 24.6 mm, annual potential evaporation ranges from 66.85 to 530 mm, the annual average minimum temperature is 9.64 degrees Celsius, and annual average maximum temperature is 35.39 degrees Celsius. The Tigris River is the primary source of water supply in the area, stretching about 53 km through the city with a slope of 6.7cm/km, while groundwater is the secondary source, particularly since 2003, and is used for domestic purposes. From oldest to youngest, there are three major geological formations with age of (Holocene, Pleistocene, and Quaternary deposits) (Jassim and Goff, 2006). Sand and gravel aquifers have been determined underground at depths of 8-20 m in the studied area (Al-Hadithi et al., 2019).

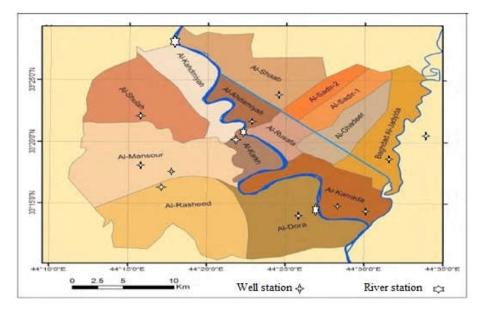


Fig.1. Map of the study area

3. Materials and Methods

3.1. Field work

During the wet (March 2021) and dry (August, 2021) seasons, a total of 15 samples were collected to determine major cations and anions, as well as stable isotopes of water (¹⁸O and ²H). 12 samples were collected from agricultural and domestic wells, and 3 samples were collected from the Tigris River throughout Baghdad. The samples for stable isotopes analysis were collected in 50mL glassy bottles at each point, while the samples for chemical analysis were collected in one-liter polyethylene bottles. A GPS device was used to obtain information about the location of the well (Trex, Garmin International Inc, USA). Electrical conductivity (EC) and pH were measured in the field using a multi-parameter device (situ). Table 1 shows the coordination, sample number, and sample positions.

Well **Elevation** Water level **Stations** Symbol Coordination's Type of Sample M depth (m) (m.s.l)Dora GW1 34 N 33 16 48.9 E 44 26 47.6 14 14 27 27 Saidia GW2 33.8 N 33 16 14.4 E 44 27 42.7 Bayaa GW3 E 44 22 27.2 33 N 33 18 56.1 26 28 Groundwater Daoudi GW4 34 N 33 19 02.4 E 44 21 54 11 11 In Al-Karkh side 10 Mansour GW5 36.6 N 33 16 10.9 E44 21 11.4 10 37 22 22 Rahmania GW6 N 33 22 19.2 E 44 17 27.0 Ghazaliya GW7 35 N 33 21 12.2 E 44 21 15.1 20 20 Zafaraniyah GW8 36 N 33 14 08.7 E 44 30 07.7 15 15 33.9 Shaab GW9 N 33 23 36.4 E 44 23 26.2 13 13 Groundwater in Twaitha GW10 31 N 33 21 41.3 E 44 21 08.6 14 14 Al-Rassafa side Jadriya GW11 35 N 33 12 17 E 44 3 52 21 21 Adhamiya **GW12** 33.9 N 33 16 43.6 E 44 23 09.3 18 18 West Tigris SW1 36 N 33 25 01.3 E 44 20 40.6 Shwhada (Tigris River) SW2 34.8 N 33 21 25.4 E 44 22 58.0 SW3 E 44 27 09.3 Dora 32 N 33 17 19.3

Table 1. The details of the sampling locations in the study area

3.2. Lab Work

Table 2 displays all of the chemical and isotopic analyses of water samples performed according to APHA (2012) and IAEA (2005). Chemical parameters were analyzed in the Environment and Water Directorate's/Ministry of Science and Technology's chemical laboratories, while isotopic analyses were done in the Water Research Isotopes Lab. Table 2. devices, equipment's for water samples analysis.

Table 2. The details of the sampling locations in the study area

Measured Parameter	Methods and equipment's	
рН		pH-meter
EC & TDS		EC meter
Ca ²⁺ , T.H and Mg ²⁺	EDTA titrimetric method	
Na^+, K^+	Flame photometric method by flame photometer (AF p100)	
HCO ³⁻ , CO ³⁻	Titration method using indicator titrated with HCl	
SO_4^2 -	UV-spectrophotometer	
Cl-	titrimetric method (silver nitrate method)	
δD and δ^{18} O	Liquid-Water Stable Isotope Analyses (LWSIA)	
oD and o O	Accuracy of measurements is <0.2 for δ^{18} O and δD	

4. Results and Discussion

4.1. Hydrochemical Characterization

The concentrations of ions in the study area vary significantly due to geological conditions, climate, and human activities. The TDS of groundwater in both sides (Al-Karkh and Russafa) ranged from 0.58 to 1.29 mg/L, and from 0.45 mg/L to 1.23 mg/L on both sides, respectively (Table 3 and 4). In general, Cl and Na⁺ had a strong correlation in the groundwater environment; the mean Cl concentration was 25.71 mg/L, which was lower than the Na⁺ concentration. The Ca-SO₄ and Ca-Na-Cl-SO₄ hydrochemical facies were determined to be the dominant hydrochemical facies of groundwater on the Al-Karkh and Al-Russafa sides, respectively, while the Ca-HCO₃ hydrochemical facies were determined the Tigris river's dominant hydrochemical facies. Human activities and geochemical processes may have caused differences in hydrochemical Facies.

Table 3. Hydrochemical parameters of water samples in the studied area, August 2021

Stations	Symbol	pН	TDS ppm	EC μs/cm	Na ²⁺ Ppm	Ca ²⁺ ppm	Mg ²⁺ ppm	K ⁺ ppm	SO ₄ = ppm	HCO ₃ - ppm	Cl - ppm
Dora	GW1	7.1	1941	2562	280	220	98	3	400	190	750
Saidia	GW2	6.7	2408	3178	288	323	180	3	300	312	1002
Daoudi	GW3	7.2	1468	1937	190	96	122	3	245	567	245
Mansour	GW4	7.1	2657	3507	270	356	180	6	1100	178	567
Bayaa	GW5	7.1	891	1176	95	112	45	5	289	234	111
Ghazaliya	GW6	7.2	1896	2502	288	156	103	4	756	278	311
Rahmania	GW7	7.6	1014	1338	55	50	28	2	656	145	78
Zafaraniyah	GW8	7.5	742	979	83	83	29	4	176	300	67
Shaab	GW9	7.1	997	1316	80	154	68	6	312	312	145
Adhamiya	GW10	7.3	2169	2863	95	432	71	5	1342	122	102
Twaitha	GW11	7.3	1424	1879	156	170	74	4	564	245	211
Jadriya	GW12	6.9	1809	2387	342	160	55	5	678	380	189
East Tigris	SW1	8.2	451	595	70	58	16	3	132	105	67
Shwhada	SW2	8.1	498	657	65	60	20	4	145	123	81
Doura	SW3	7.9	553	729	70	68	25	7	156	134	93

Table 4. Hydrochemical parameters of water samples in the studied area, March, 2021

Stations	Symbol	pН	TDS	EC	Na ²⁺	Ca ²⁺	Mg ²⁺	K ⁺	SO ₄ =	HCO ₃ -	Cl-
	-	_	ppm	μs/cm	Ppm	ppm	ppm	ppm	ppm	ppm	ppm
Dora	GW1	6.9	1886	2487	272.	213	95	2.9	388	184	729
Saidia	GW2	6.5	2340	3086.	279	313	175	2.9	291	302	974
Daoudi	GW3	7.0	1426	1881	184	93	118	2.9	237	549	238
Mansour	GW4	6.9	2582	3405	262	345	175	5.8	1067	172	551
Bayaa	GW5	6.9	866	1142	92	108	44	4.8	280	226	108
Ghazaliya	GW6	7.0	1842	2430	279	151	100	3.9	733	269	302
Rahmania	GW7	7.4	985	1299	53	48	27	1.9	636	140	75
Zafaraniyah	GW8	7.3	721	951	80	81	28	3.9	170	291	65
Shaab	GW9	6.9	969	1277	75	149	66	5.8	302	302	141
Adhamiya	GW10	7.1	2108	2780	92	419	69	4.8	1301	118	99
Twaitha	GW11	7.1	1384	1825	151	165	72	3.9	547	237	205
Jadriya	GW12	6.7	1758	2318	332	155	53	4.8	657	369	183
East Tigris	SW1	8.0	438	578	68	56	16	2.9	128	101	65
Shwhada	SW2	7.9	484	638	63	58	19	3.9	140	119	78
Doura	SW3	7.7	537	708	68	65	22	6.8	151	129	90

In the month of March 2021, the pH of water ranges from 6.5 to 8, with an average electrical conductivity of 1811 μ s/cm and a range of 578 to 3045 μ s/cm. TDS has an average concentration of 1373 mg/L with a range of 338 to 2582 mg/L. The concentrations of Na and Cl range from 53 to 332 and 65 to 974 mg/L, respectively. HCO₃ has an average value of 245 mg/L and a range of 104 to 549.46 mg/L. Ca²⁺ (48-416 mg/L) and Mg²⁺ (15-174 mg/L) concentrations in groundwater samples ranged (from1.9 to 6.8 mg/L) compared to SO₄ ²⁻ (128-1301 mg/L), K⁺ concentrations in groundwater samples ranged

(from 1.9 to 6.8 mg/L). The variation of TDS, Cation and Anions in the study area for both periods as shown in Figs. 2 and 3).

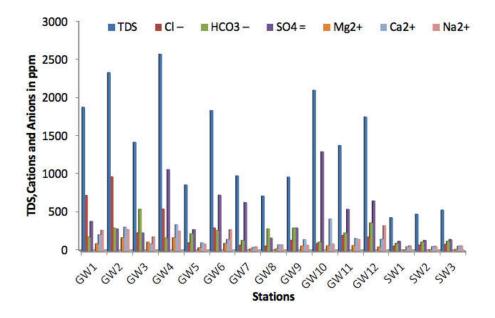


Fig. 2. Variation of TDS values and ions concentration for dry period in the study area

In the month of August 2021, The pH of water ranges from 6.7 to 8.2. It has an average electrical conductivity of 1811 μ s/cm and a range of 595 to 3507 lS/cm. TDS levels average 1413 mg/L and range from 451 to 2657 mg/L. The concentrations of Na and Cl range from 55 to 342 and 67 to 1002 mg/L, respectively. HCO₃ - has an average value of 252 mg/L and a range of 101 to 567 mg/L. Ca²⁺ (50-432 mg/L) and Mg²⁺ (16-180 mg/L) concentrations were compared to SO4 2- (132-1342 mg/L), and K⁺ concentrations in groundwater samples ranged from 2 to 7 mg/L. Again, the concentrations are very low in comparison to other substances.

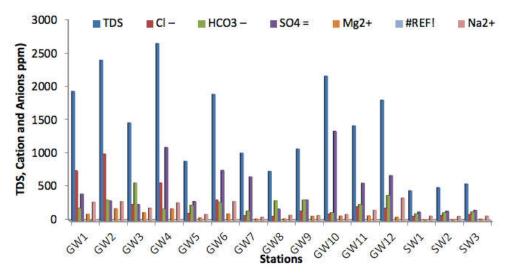


Fig. 3. Variation of TDS values and Ions concentration for dry period in the study area

The Gibbs diagram is commonly used to assess the source of dissolved chemical components, such as precipitation dominance, rock dominance, and evaporation. (Gibbs 1970). This graph depicts the Cl⁻/(Cl⁻+HCO₃⁻) ratio as a function of TDS (Fig. 4). The distribution of sample points indicates that the chemical weathering of rock-forming minerals has an impact on groundwater quality. Except for GW3 and GW4, the majority of the samples are influenced by rock dissolution.

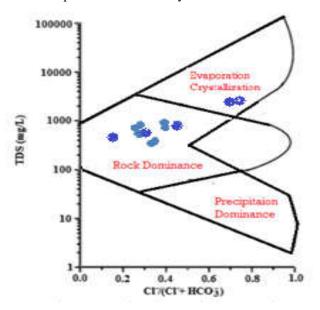


Fig. 4. Gibbs Diagram describes the study area

4.2. Source of Salinity

In the study area, the chemical analysis of the water samples revealed that the salinity ranges from 0.35 to 2.13 in March and 0.36 to 2.19 in August, 2021. Mansour station has the highest salinity of 2.19 and 2.13 (depth of 10 m), while Bayaa station has the lowest salinity of 0.73 and 0.70. The salinity gradient is increasing from the Russafa side to the Karkh side. However, groundwater salinity increased towards the study area's right side, which is similar to the spatial distribution pattern of electrical conductivity EC and Cl $^{-}$ concentrations. The majority of high salinity water is found at depths ranging from 10 to 100 meters. The potential salinization sources in different depth groundwater in the study area are diverse, including natural saline and the presence of wastewater. (Krishnan,1985), As a result, the evaporation process at high temperatures could be a possible source of the different depths of groundwater salinity in the study area. Fig. 5 shows that three distinct groups of water are identified based on EC values and the hydrological setting: (1) Group A refers to well waters with EC values of were 2000µs/cm. (2) Waters collected from wells are assigned to Group B. these waters have EC values ranging from 1000 to 2000 µs/cm. (3) Group C represents water samples collected from the Tigris River. these waters have EC values that are less than 1000µs/cm.

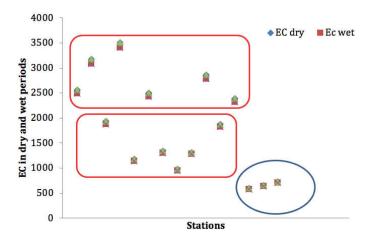


Fig. 5. Three groups were distinguished depending on EC values for two periods.

4.3. Isotopic Content

Locally, many researchers were exploring and develop isotopic tools that can be used to determine salinity sources and processes in aquifer systems. (Al-Paruany, 2013; Ajeena, 2014 Al-Paruany, 2017, Al-Kafaghi 2018, Nada, 2020, Ibraheem, 2020). To study the origin and mineralization of groundwater, 12 wells and three sample of Tigris River were subjected of isotopic studies (Table 5, 6). The values of δ ¹⁸O in wells samples range from -6.46 to -3.99‰. and the δ ²H ranges between -39.9 and 26.6‰, in wet period (March, 2018) While The values of δ ¹⁸O in wells samples range from -7.0 to -4.2‰, and the δ ²H ranges between -40 and 28‰, in wet period (Agust, 2018). The isotope values of the Tigris River in March are from -36.7‰ to -34.5 for δ ²H and -6.62‰ to -6.34 for δ ¹⁸O, while The isotope values of the Tigris River in August are from -39.9‰ to -37.5 for δ ²H and from -7.2‰ to -6.9 for δ ¹⁸O. Stable isotope values of water are represented graphically in Fig. 6 in comparison with the Global Meteoric Water Line (GMWL) defined by Craig (1961), with δ ²H = 8 × δ ¹⁸O + 10 and the Iraqi Meteoric Water Line (IMWL) define by Al-Paruany (2013), with δ ²H = 7.573 × δ ¹⁸O + 13.97.

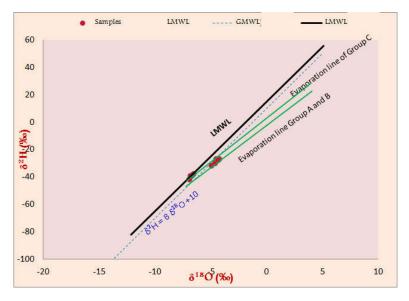


Fig. 6. Relationship of δ^{18} O and δ^{2} H values of groundwater samples in the area compared with the Iraq meteoric water line (IMWL) and global meteoric water line (GMWL).

Stations	Symbol	δ ¹⁸ O‰	δD%0	Symbol	Station	δ^{18} O‰	δD‰
Dora	GW1	-6.3717	-37.05	SW1	East Tigris	-6.532	-35.88
Saidia	GW2	-4.2795	-25.65	SW2	Shwhada	-6.348	-34.5
Daoudi	GW3	-4.6599	-30.4	SW3	Doura	-6.624	-36.708
Mansour	GW4	-4.1844	-26.6				
Bayaa	GW5	-4.3746	-28.5				
Ghazaliya	GW6	-3.9942	-25.65				
Rahmania	GW7	-6.44778	-37.05				
Zafaraniyah	GW8	-6.5619	-39.9				
Shaab	GW9	-4.0893	-26.6				
Adhamiya	GW10	-6.1815	-36.1				
Twaitha	GW11	-6.657	-38				
Jadriya	GW12	-6.4668	-37.05				

Table 6. Isotopic content of water samples in the study area (groundwater, Tigris river), March, 2021

Stations	Symbol	δ^{18} O%0	δD%0	Symbol	Station	δ ¹⁸ O‰	δD%0
Dora	GW1	-6.7	-39	SW1	East Tigris	-7.1	-39
Saidia	GW2	-4.5	-27	SW2	Shwhada	-6.9	-37.5
Daoudi	GW3	-4.9	-32	SW3	Doura	-7.2	-39.9
Mansour	GW4	-4.4	-28				
Bayaa	GW5	-4.6	-30				
Ghazaliya	GW6	-4.2	-27				
Rahmania	GW7	-6.78	-39				
Zafaraniyah	GW8	-6.9	-42				
Shaab	GW9	-4.3	-28				
Adhamiya	GW10	-6.5	-38				
Twaitha	GW11	-7	-40				
Jadriya	GW12	-6.8	-39				

Fig 7 shows that there are minor variations of isotopic values in the studied area. Three distinct groups are distinguished, Waters in groups A and B vary seasonally, from depleted values in March to enriched values in August, as shown on the ² H vs. ¹⁸O diagram, due to mixing with surface water and the effect of sewage water. Group C waters are depleted in March and more enriched in August, and they are influenced by sewage or agricultural water. Isotope results from the study area confirm the presence of at least three salinity sources in the collected samples: old water; dissolution from Holocene, and Pleistocene deposits; and anthropogenic pollution.

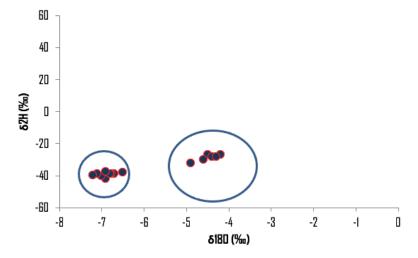


Fig. 7. Group A&B mixing and Group C depend on Isotopic content in the study area

The ¹⁸O/SO₄ diagram clearly shows that there is no correlation between sulfate SO₄ and ¹⁸O in water. Because sulfates formed by oxidation of sulfides should show a relationship between ¹⁸O-SO₄ and ¹⁸O-H₂O, this indicates the absence of Sulphide oxidation. There is no correlation between the values of ¹⁸O and SO₄ in this study, so we conclude that the values of ¹⁸O sulfate in water depend on the source of sulfate rather than water. The isotopic composition of groundwater from wells and the Tigris River differs insignificantly (Fig.8).

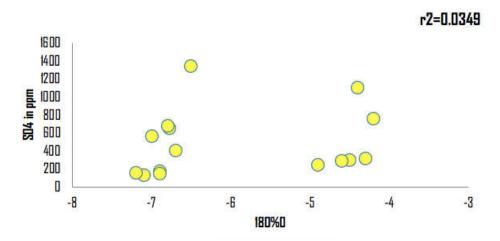


Fig. 8. The relation between SO₄ and ¹⁸O in the study area.

The deuterium excess (d-excess) as one of the useful tools for studying water vapor sources, such as vapor source humidity or evaporation effect during rainfall (Clark and Fritz, 1997; Al-Paruany (2013) studied the d-excess in Iraq and found that the precipitation in Iraq has distinct seasonal variation in d-excess values, with high (d 16.9) and low (d >10.4) values. Fig. 9 depicts all of the d-excess sample values in the study area.

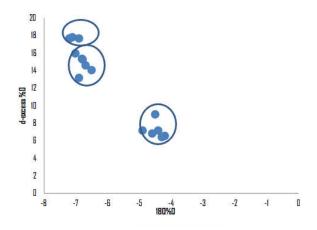


Fig. 9. Distribution of d-excess in the study area

To determine the source of salinity in water samples from the study area. by discussing the relationship between ¹⁸O and EC, stable isotopes can successfully determine the mechanisms of groundwater salinization and identify the source of salinity. The origin of salinization from salt dissolution is not associated with any significant changes in the stable isotopic composition, but the mixing and/or evaporation processes are invariably associated with sensitive changes in the stable isotopic composition (Blackburn and Mcleod, 1983; IAEA, 2001).

According to Fig 10, The lack of significant differences between ¹⁸O values and EC values may indicate that the source of salinity in the study area is due to mixing and/or dissolution processes. It is clear that some well water in the study area had the same values of ¹⁸O (-6.9-6) with nearby in salinity values during the studied periods. This can be attributed to the influences of dissolution, mixing with sewage, and water sink. Some of these resources are natural, while others are man-made (Al-charideh, 2010).

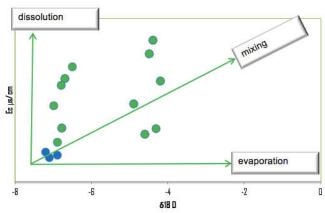


Fig. 10. The relationship between ¹⁸O and EC values in the study area

Finally, it is clear that dissolution and mixing processes are the most important factors that affect the source of salinity, as well as the major factor that is related to human activity (mixing with swage water).

5. Conclusions

 Hydrochemical and stable isotope techniques were used in this study to investigate the source of salinity in some wells in Baghdad. The following are the main findings of this study:

- The Ca-SO₄ and Ca-Na-Cl-SO₄ hydrochemical facies were found to be the dominant hydrochemical facies of groundwater on the Al-Karkh and Al-Russafa sides, respectively, while the Ca-HCO₃ hydrochemical facies were found to be the dominant hydrochemical facies of the Tigris River.
- Human activities and geochemical processes may have caused differences in hydrochemical Facies.
- Three distinct groups of water are identified based on EC values and the hydrological setting: (1) Group A refers to well waters with EC values of up to 2000s/cm. (2) Waters collected from wells are assigned to Group B. The EC values of these water range less than 1000µs/cm.
- Isotope results from the study area confirm the presence of at least three salinity sources in the collected samples: old water, dissolution from Holocene and Pleistocene deposits, and anthropogenic pollution.
- companion the hydrochemical and isotopic techniques to study the origin of salinity in the studied area, it's clear results that, dissolution, mixing process are most factors that affect the source of salinity, as well as the major factor that is related to human activity (mixing with swage water).

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