



## Water Chemistry and Soil Type as Key Factors in Ion Pair Formation.

kazhin Sarbaz Rajab

Department of Soil and Water, College of Agriculture Engineering Sciences, University of Salahaddin-Erbil, IRAQ.

\*Corresponding Author: [kazhin.rajab@su.edu.krd](mailto:kazhin.rajab@su.edu.krd).

Received: 29/03/2025

Revised: 20/05/2025

Accepted: 25/05/2025

Published: 01/06/2025

### ABSTRACT

Water samples were taken from 36 wells in agricultural lands in Erbil governorate, Iraqi Kurdistan region. Soil samples were taken from five calcareous and seven gypsiferous soils from different locations in the Erbil and Nineveh governorates. Some of the chemical properties of the studied waters and soils were analyzed. Then, the water types, soil types, ion pairs, and their activities and ionic strengths were calculated. The main results were summarized as follows:

The water of (11, 10, 9, 2, 2, and 2) wells before correcting ion pairs plus activity had (Ca-SO<sub>4</sub>, Ca-HCO<sub>3</sub>, Mg-SO<sub>4</sub>, Mg-HCO<sub>3</sub>, Na-HCO<sub>3</sub>, Na-SO<sub>4</sub>) types, respectively. After correcting ion pairs and activity, the water of (1, 16, 3, 6, 7, and 3) wells had the mentioned types, which means correcting ion pairs and activity had a great impact on changing the water types.

The soil samples represent seven gypsiferous and five calcareous soils, depending on their calcium carbonate and gypsum content. The amount of ion pairs in gypsiferous soils is higher than their amount in calcareous soils. The ratio between ion pairs in gypsiferous to calcareous soil ranged from 0.67 to 3.19. The highest value was recorded for (CaSO<sub>4</sub>)<sup>0</sup>, while the lowest value was for (MgHCO<sub>3</sub>)<sup>0</sup>. The series of ion pairs for both gypsiferous and calcareous soils was arranged as [(CaSO<sub>4</sub>)<sup>0</sup>, (MgSO<sub>4</sub>)<sup>0</sup>, (CaHCO<sub>3</sub>)<sup>+</sup>, (MgHCO<sub>3</sub>)<sup>+</sup>, (NaSO<sub>4</sub>)<sup>-</sup>, (KSO<sub>4</sub>)<sup>-</sup>, and (NaHCO<sub>3</sub>)<sup>0</sup>]. The dominant ions contributing to ion pair formation are Ca<sup>+2</sup> and SO<sub>4</sub><sup>-2</sup>; their highest and lowest values were recorded at Sinul and Akri locations, respectively. The highest correlation coefficient value between ionic strength and ion pairs was recorded in gypsiferous soil compared with calcareous soil, with the mean values of correlation coefficient of (r= 0.71\*\* and 0.54\*), respectively.

**Keywords:** Water chemical composition, Groundwater, Ionic strength, Calcareous soil, Gypsiferous soil.

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### INTRODUCTION

Groundwater is pivotal in agriculture as it is increasingly used for irrigation. The growing population and recent climate change are putting water resources under pressure worldwide, calling for new water planning and management approaches if escalating conflicts are avoided and environmental degradation is reversed. In arid and semi-arid areas, the dependency on groundwater for water supply is between 60 and 100% [1], especially in those regions that are subject to low and irregular precipitation.

Irrigation and agricultural uses are considered to be the most intensive water consumers, and they require 66% of demand across the region [2], consequently, the water shortage problem cannot be accurately analyzed without a thorough consideration of agriculture in the region [3].

Water quality in the Kurdistan region varies from one location to another, depending on the geological formation of the study area, the chemical composition of the aquifer, environmental conditions, etc. [4]. A large basin of groundwater exists in the Erbil governorate, which covers an area of more than 5000 km<sup>2</sup>, compared to the area of groundwater basins in other governorates of the Iraqi Kurdistan region. The number of drilled wells is 9805 wells [4]. The farmers in the Kurdistan region depend mainly on groundwater for irrigation and agricultural uses due to the shortage or absence of irrigation projects and the construction of numerous dams on the Tigris and Euphrates in the riparian nations.

Some soluble anions and cations in water or soil solution will approach to each other for a distance equal or less than 5 angstroms by columbic force and both of them are keeping its hydration shell and differing in charge type (positive and negative charge) this phenomenon called ion pairing [5] and [6]. The ion pair charge depends upon the valence of the contributed anion and cation in ion pairs, if the ions are of equal but opposite charge, the ion pair will be uncharged like (CaSO<sub>4</sub>)<sup>0</sup> and (MgSO<sub>4</sub>)<sup>0</sup> ion pairs, if the ions are of unequal charge, the ion- pair will have negative or positive charge such as (KSO<sub>4</sub>)<sup>-</sup>, and (CaHCO<sub>3</sub>)<sup>+</sup> ion pairs.

The chemical composition of irrigation water and soil type had a significant influence on the type and amount of ion pair formation in water and soil solution [7]. Since there are little or no investigations about the impacts of water and soil types on amount and types of ion pairs, for these reasons, this study focused on:

- 1- The role of water types and chemical composition in forming different ion pairs.
- 2- Influences of soil types on the amount and types of ion pairs.

## Materials and methods

### 3.1. Study area description

The study area is located in Erbil and some locations in the Nineveh Governorate. The study area included the water type of 36 wells (Figure 1) and some agricultural lands, which included calcareous and gypsiferous soils (Figure 2).

### 3.2. Water and Soil sampling

Water samples were collected from 36 wells in the Erbil governorate. The depth of the wells ranged between 150- 300 m as recorded from the history of wells and permissions of wells drilling. The water samples were taken by using a plastic bottle of 1000 ml, then kept in the refrigerator at (4 °C) and then sent to the laboratory for analysis.

Soil samples were taken from different locations in the Erbil and Nineveh governorates, representing calcareous and gypsiferous soils, as shown in (Figure 2).

### 3.3. Water and Soil Analysis

The water and soil chemical analysis included EC, pH, and the concentration of  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$  in addition to the determination of soil  $\text{CaCO}_3$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  according to standard methods mentioned by [8] and [9]. The pH-meter, EC-meter, and flame photometer were calibrated before use according to the methods mentioned by [8]. The results of water and soil analyses were recorded in Tables 1 and 2. The water and soil types were determined depending on the dominant cations and anions for each water and soil sample as recorded from the mentioned tables. Ion pairs, ionic activity, type of ion pairs, amount of ion pairs, and the number of ions contributed to ion pairing were determined according to [10], which converted the data to  $\text{mmol L}^{-1}$  in the applied program.

### 3.4. Water and Soil Type

The water and soil types were calculated using the dominant cation and anion in  $\text{mmol}_e \text{L}^{-1}$  for the studied water and soil samples [4].

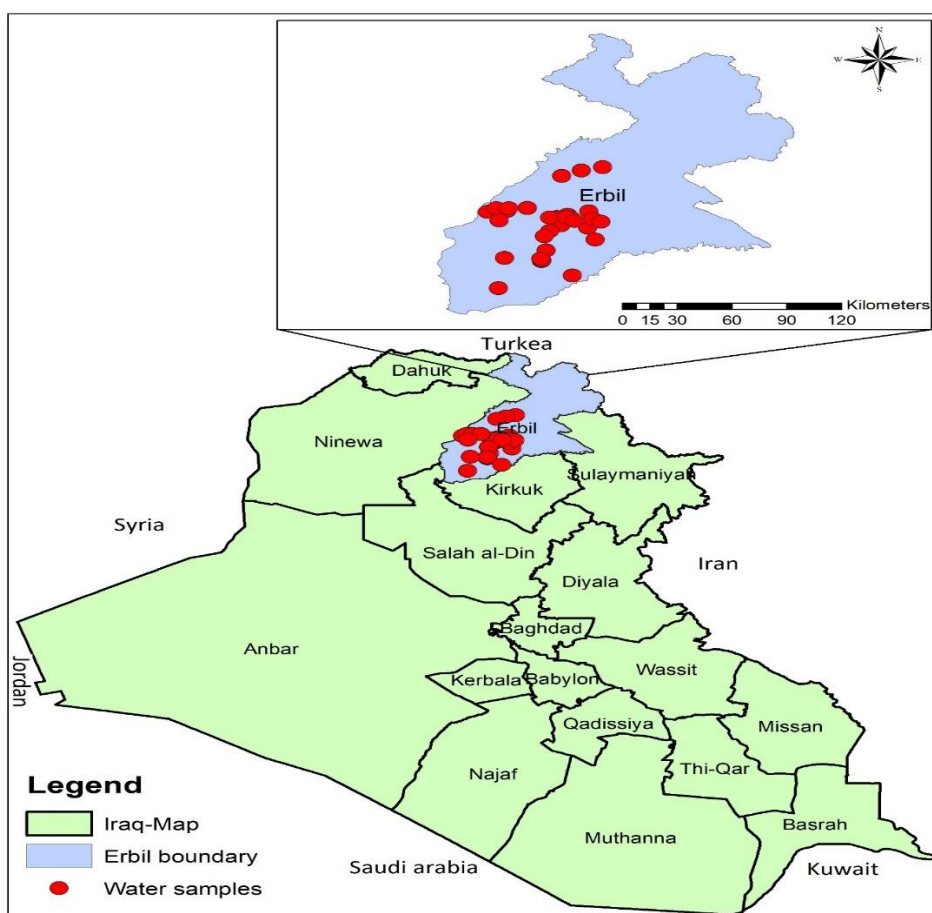


Figure 1: Locations of the studied water samples

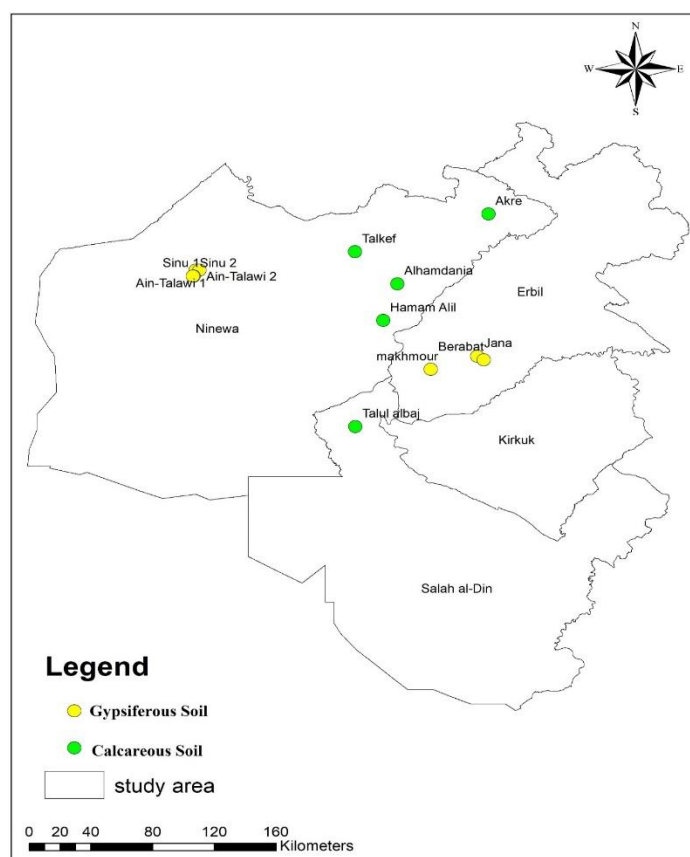


Figure 2: Location of the studied soil samples

Table 1: Some chemical properties of the study water sample

Locations	EC dS m <sup>-1</sup>	pH	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SO <sub>4</sub> <sup>-2</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>
			mmol <sub>c</sub> L <sup>-1</sup>						
Mzahmad	0.55	7.43	2.90	1.58	0.98	0.03	0.91	3.74	0.49
Qoritan 1	0.32	7.87	2.01	2.40	0.17	1.20	1.89	1.23	0.40
Qoritan 2	0.41	7.26	2.45	1.32	0.41	0.02	0.25	3.30	0.35
Pirdawd 1	0.73	8.03	4.11	3.00	0.40	0.01	3.74	2.79	0.87
Pirdawd 2	0.71	7.37	3.39	2.34	1.19	0.03	2.46	3.77	0.71
Quchabilbas 1	0.56	7.61	2.60	2.31	0.65	0.02	2.20	2.51	0.88
Haje Aleawa	0.65	7.56	3.96	1.97	0.60	0.02	2.55	3.09	0.41
Daldghan	0.72	7.19	3.41	2.58	1.05	0.03	1.61	4.89	0.43
Cheman	0.87	7.30	3.35	3.47	1.74	0.03	3.53	3.96	1.22
Chaltwk	1.04	7.38	3.58	3.54	5.04	0.05	3.79	4.19	0.98
Alla	1.13	7.18	3.76	4.12	3.18	0.06	3.22	4.14	1.45
Mastawa Shekhan	1.19	7.04	7.74	2.55	3.19	0.03	5.03	6.92	0.70
Kandarakal	0.40	7.69	1.56	0.78	1.64	0.02	1.41	2.17	0.44
Qara chnagha	1.07	7.51	4.46	5.02	1.17	0.08	6.07	3.25	1.41
Yadaqzlar 1	1.07	7.32	3.71	5.46	1.50	0.03	5.03	4.51	1.15
Yadaqzlar 2	2.85	7.48	10.56	11.46	6.43	0.08	22.70	2.64	3.20
Gabalak	7.04	7.56	25.45	22.51	22.02	0.44	46.34	2.18	21.90
Grdachal 1	7.57	7.40	23.94	21.47	30.08	0.22	40.63	1.94	33.14
Grdachal 2	1.02	7.80	4.80	3.89	2.21	0.01	5.90	4.00	1.05
Abo Sheta	0.21	7.86	1.00	0.99	0.28	0.01	1.11	0.81	0.38

Zaga	0.31	7.84	1.50	1.24	0.68	0.01	1.40	1.60	0.44
Qadria	1.79	7.85	6.98	9.78	2.60	0.01	8.80	7.72	3.21
Hawera	1.23	7.87	5.34	2.80	4.39	0.01	7.00	4.30	1.30
Klaw Rash	1.13	8.05	4.45	3.75	3.23	0.02	5.73	4.00	1.67
Kapran	2.35	7.95	12.20	11.00	0.50	0.01	6.40	11.43	5.96
Alyawa	3.32	7.56	14.20	12.60	8.22	0.02	17.80	12.34	4.35
Karasur 1	4.01	7.53	20.00	12.88	8.90	0.03	19.00	17.06	5.00
Karasur 2	3.32	7.55	11.45	12.55	10.32	0.04	15.45	12.39	6.97
Kalshkhan	4.24	7.63	17.50	18.33	7.50	0.04	20.20	15.03	8.38
Mehedi	4.05	7.33	18.00	14.45	12.31	0.08	19.09	15.55	7.00
Kndal	2.92	7.40	12.56	10.68	7.75	0.03	15.20	12.00	4.11
Sargran	0.57	7.91	2.78	2.11	1.02	0.01	2.80	2.00	1.19
Qushtapa	0.35	7.93	2.00	1.90	0.37	0.01	1.70	2.11	0.43
Murtakagawra	0.39	7.91	2.01	2.02	0.17	0.01	2.00	1.70	0.42
Sablagh	0.41	7.99	1.80	2.44	0.17	0.01	2.39	1.20	0.65
Quchabilbas 2	1.72	7.59	7.11	6.27	4.44	0.08	8.66	5.34	3.44
Mean	1.81	0.28	6.68	6.01	6.34	0.21	10.69	4.50	6.45

\*mmol<sub>c</sub> L<sup>-1</sup> = meq L<sup>-1</sup> and mmol L<sup>-1</sup> = mmol<sub>c</sub> L<sup>-1</sup> / Valence, which is used in determining ion pairs and activity.

Table 2: Some chemical properties of the study soil sample

Locations	Soil type	EC dS m <sup>-1</sup>	pH	Ca <sup>+2</sup> mmol <sub>c</sub> L <sup>-1</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	SO <sub>4</sub> <sup>-2</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Ionic strength mole L <sup>-1</sup>	CaCO <sub>3</sub> g kg <sup>-1</sup>	CaSO <sub>4</sub> .2H <sub>2</sub> O
Ain-Talawi 1	Gypsiferous Soil	5.08	7.73	62.00	7.50	1.295	0.25	65.65	2.80	2.60	0.087	235.66	321.56
Ain-Talawi 2		4.80	7.85	60.00	5.00	0.24	0.27	60.72	3.60	1.20	0.081	192.08	250.27
Sinu 1		5.19	7.68	61.80	7.70	0.83	0.21	65.73	3.40	1.40	0.086	162.76	597.20
Sinu 2		4.40	7.81	56.70	4.20	0.21	0.24	55.32	3.30	2.50	0.076	162.20	235.32
makhmour		1.52	7.19	2.51	0.81	3.31	0.49	7.23	0.45	0.38	0.011	82.00	239.00
Jana		0.85	7.90	5.51	2.10	0.50	0.30	7.20	1.00	1.50	0.014	160.23	220.21
Berabat		0.72	8.10	3.98	2.50	0.50	0.21	4.10	1.30	1.70	0.011	178.25	198.56
Talkef	Calcareous Soil	1.07	8.02	5.95	4.64	0.55	0.27	4.41	3.31	1.14	0.047	235.00	16.20
Alhamdania		1.34	7.70	7.83	5.63	0.66	0.09	5.24	3.02	1.39	0.006	230.00	12.34
Talul al baj		3.55	7.76	30.06	6.05	1.04	0.86	30.38	2.93	0.78	0.015	146.02	43.36
Hamam Alil		3.35	7.85	33.46	1.99	0.21	0.41	29.38	2.52	2.00	0.018	204.95	45.37
Akre		0.41	7.73	0.39	0.25	2.55	0.11	4.23	0.15	0.28	0.048	234.00	38.00
Mean		2.69	7.78	27.52	4.03	0.99	0.31	28.30	2.32	1.41	0.04	185.26	184.78
SD		1.88	0.22	26.22	2.49	0.98	0.21	26.52	1.24	0.73	0.03	46.46	170.34

## Results and discussion:

Table 3 shows the range and mean of chemical properties of the study water samples before and after correcting ion pairs and activity. It is regarded as a database for limiting water types and the influence of correcting ion pair plus activity on water type conversion.

Table 3: Range and mean of the chemical properties of water samples before and after correcting ion pairs plus activity

Chemical properties	Unit	Range	Mean $\pm$ SD	Range	Mean $\pm$ SD	Activity coefficient
		Before correcting ion pairs		After correcting ion pairs and activity		
EC	dS m <sup>-1</sup>	0.21-7.57	1.71 $\pm$ 1.76	0.21 - 7.57	1.71 $\pm$ 1.76	
pH		7.04 - 8.05	7.58 $\pm$ 0.28	7.04 - 8.05	7.58 $\pm$ 0.28	
Ca <sup>+2</sup>		1.00 - 25.45	7.05 $\pm$ 6.51	0.73 - 7.26	2.95 $\pm$ 1.93	0.53
Mg <sup>+2</sup>		0.78 - 22.51	6.14 $\pm$ 5.87	0.54 - 7.11	2.76 $\pm$ 1.99	0.55
Na <sup>+</sup>		0.17 - 30.08	4.38 $\pm$ 6.17	0.16 - 23.15	3.63 $\pm$ 4.91	0.87
K <sup>+</sup>		0.01 - 1.20	0.08 $\pm$ 0.20	0.01 - 0.32	0.04 $\pm$ 0.06	0.86
CO <sub>3</sub> <sup>-2</sup>	mmol L <sup>-1</sup>	N. D	N. D	N. D	N. D	N. D*
HCO <sub>3</sub> <sup>-</sup>		0.81 - 17.06	5.43 $\pm$ 4.38	0.75 - 12.88	4.39 $\pm$ 3.34	0.85
SO <sub>4</sub> <sup>-2</sup>		0.25 - 46.34	8.49 $\pm$ 10.42	0.15 - 11.38	2.99 $\pm$ 2.67	0.48
Cl <sup>-</sup>		0.35 - 33.14	3.37 $\pm$ 6.28	0.35 - 33.14	3.37 $\pm$ 6.28	
Ionic strength	mole L <sup>-1</sup>	0.004 - 0.09	0.02 $\pm$ 0.02	0.004 - 0.09	0.02 $\pm$ 0.02	Activity coefficient = activity/concentration

\* N.D. = Not detected

Table (4) illustrates that the water of (11, 10, 9, 2, 2, and 2) wells had (Ca-SO<sub>4</sub>, Ca-HCO<sub>3</sub>, Mg-SO<sub>4</sub>, Mg-HCO<sub>3</sub>, Na-HCO<sub>3</sub>, Na-SO<sub>4</sub>) types respectively before correcting ion pairs and activity. This means that the highest number of the study waters had Ca-SO<sub>4</sub> type, and the lowest number of well waters had Na-SO<sub>4</sub> type. This may be due to the variation in the chemical composition of the study water samples (Table 1) and their contribution in ion pairs (Tables 5 and 6) due to the difference in the geological formation of the studied locations [11 and 12].

Correcting ion pairs and activity caused the change in water types as shown in Table 4, which caused an increase and decrease in water types; for example, the water samples had types Ca-SO<sub>4</sub> and Mg-SO<sub>4</sub> decrease from 11 to 1 and 9 to 3 waters, respectively. It means the water for 11 and 9 wells had Ca-SO<sub>4</sub> and Mg-SO<sub>4</sub> type before correcting ion pairs and activity, while after correction, only the water for 1 and 3 wells had the mentioned types, respectively (Table 4). These resulted from high contribution of Ca<sup>+2</sup> and SO<sub>4</sub><sup>-2</sup>, with the range (0.032 - 4.037) and (0.018 - 7.794) mmol L<sup>-1</sup> in ion pairing respectively (Table 6). On the other hand, the number of waters had types of (Ca-HCO<sub>3</sub>, Mg-HCO<sub>3</sub>, Na-HCO<sub>3</sub>, Na-SO<sub>4</sub>) increased after correcting ion pairs and ion pairs plus activity from (10 to 16), (2 to 6), (2 to 7), and (2 to 3) water samples respectively (Table 5). This is because of the contributing low amount of monovalent ions in ion pairs in comparison with divalent ions (Table 6 and 7). The type of ion pairs was (CaSO<sub>4</sub>)<sup>0</sup>, (CaHCO<sub>3</sub>)<sup>+</sup>, (MgSO<sub>4</sub>)<sup>0</sup>, (MgHCO<sub>3</sub>)<sup>+</sup>, (NaSO<sub>4</sub>)<sup>-</sup>, (NaHCO<sub>3</sub>)<sup>0</sup>, (KSO<sub>4</sub>)<sup>-</sup> with the mean of (0.626, 0.158, 0.544, 0.116, 0.046, 0.011, 0.001) mmol L<sup>-1</sup> respectively (Table 5), while the mean of ions contributed in ion-pairing was (0.784, 0.661, 0.057, 0.001, 0.285 and 1.218) mmol L<sup>-1</sup>, for (Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+</sup>, K<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-2</sup>) respectively (Table 6). These changes in water types occurred after correcting for ion pairs and activity (Table 4).

Figures 3 and 4 illustrate the spatial distribution of water types before and after correcting for ion pairs and activity.

Table 4: Water types for the studied groundwater before and after correcting ion pairs and activity

Water type before correcting ion pairs and activity	Number of water types	Water type after correcting ion pairs and activity	Number of water types	Change in no. of water types (+=Increase, -=decrease)
Ca-SO <sub>4</sub>	11	Ca-SO <sub>4</sub>	1	-10
Ca-HCO <sub>3</sub>	10	Ca-HCO <sub>3</sub>	16	+6
Mg-SO <sub>4</sub>	9	Mg-SO <sub>4</sub>	3	-6
Mg-HCO <sub>3</sub>	2	Mg-HCO <sub>3</sub>	6	+4
Na-HCO <sub>3</sub>	2	Na-HCO <sub>3</sub>	7	+5
Na-SO <sub>4</sub>	2	Na-SO <sub>4</sub>	3	+1
Sum of water samples	36		36	

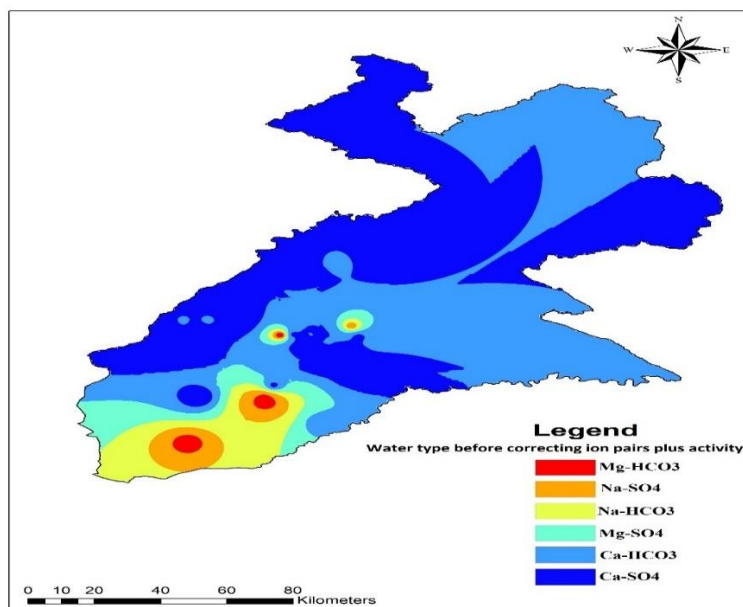


Figure 3: Spatial distribution of water types before correcting ion pairs and activity

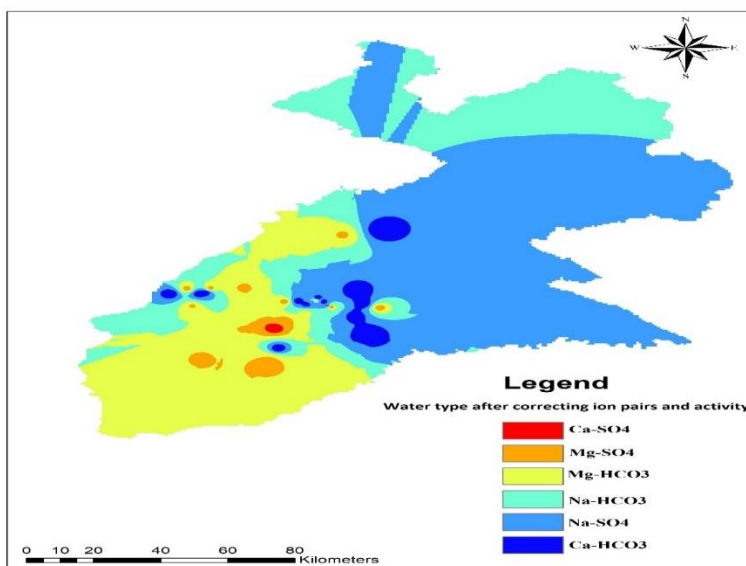


Figure 4: Spatial distribution of water type after correcting ion pairs and activity

Table 5: Amount and types of ion pairs in water samples (mmol L<sup>-1</sup>)

Locations	(CaSO <sub>4</sub> ) <sup>0</sup>	(CaHCO <sub>3</sub> ) <sup>+</sup>	(MgSO <sub>4</sub> ) <sup>0</sup>	(MgHCO <sub>3</sub> ) <sup>+</sup>	(NaSO <sub>4</sub> ) <sup>-</sup>	(NaHCO <sub>3</sub> ) <sup>0</sup>	(KSO <sub>4</sub> ) <sup>-</sup>
Mzahmad	0.048	0.058	0.024	0.026	0.001	0.002	0
Qoritan 1	0.071	0.013	0.078	0.013	0	0	0.006
Qoritan 2	0.012	0.046	0.006	0.02	0	0.001	0
Pirdawd 1	0.13	0.061	0.083	0.035	0.003	0.002	0
Pirdawd 2	0.078	0.077	0.052	0.046	0.002	0.002	0
Quchabilbas 1	0.028	0.058	0.014	0.026	0	0.001	0
Haje Aleawa	0.159	0.06	0.073	0.024	0.002	0.001	0

Daldghan	0.086	0.081	0.06	0.051	0.002	0.002	0
Cheman	0.165	0.059	0.159	0.051	0.006	0.003	0
Chaltwk	0.177	0.064	0.163	0.053	0.018	0.009	0
Alla	0.159	0.068	0.162	0.062	0.009	0.006	0
Mastawa Shekhan	0.428	0.209	0.132	0.058	0.013	0.009	0
Kandarakal	0.300	0.091	0.292	0.079	0.042	0.018	0.001
Qara chnagha	0.046	0.019	0.021	0.008	0.003	0.002	0
Yadaqzlar 1	0.317	0.058	0.334	0.055	0.006	0.002	0.001
Yadaqzlar 2	0.224	0.069	0.308	0.084	0.007	0.003	0
Gabalak	1.465	0.073	1.528	0.068	0.088	0.006	0.002
Grdachal 1	3.934	0.103	3.440	0.080	0.403	0.015	0.017
Grdachal 2	3.301	0.088	2.932	0.07	0.474	0.018	0.007
Abo Sheta	0.337	0.077	0.255	0.052	0.011	0.004	0
Zaga	0.027	0.005	0.024	0.004	0	0	0
Qadria	0.045	0.014	0.034	0.009	0.001	0.001	0
Hawera	0.51	0.179	0.679	0.213	0.016	0.008	0
Klaw Rash	0.424	0.088	0.209	0.039	0.027	0.008	0
Kapran	0.305	0.072	0.240	0.050	0.016	0.005	0
Alyawa	0.565	0.447	0.486	0.344	0.002	0.002	0
Karasur 1	1.417	0.452	1.219	0.347	0.08	0.036	0
Karasur 2	1.870	0.820	1.176	0.460	0.084	0.052	0.001
Kalshkhan	1.043	0.377	1.107	0.357	0.090	0.046	0.001
Mehedi	1.669	0.624	1.707	0.570	0.072	0.038	0.001
Kndal	1.679	0.672	1.316	0.470	0.115	0.065	0.002
Sargran	1.175	0.410	0.964	0.300	0.068	0.034	0.001
Qushtapa	0.129	0.027	0.090	0.017	0.003	0.001	0
Murtakagawra	0.065	0.023	0.056	0.018	0.001	0	0
Sablagh	0.076	0.018	0.070	0.015	0	0	0
Quchabilbas 2	0.079	0.011	0.098	0.013	0	0	0
Mean	0.626	0.158	0.544	0.116	0.046	0.011	0.001
SD	0.919	0.208	0.812	0.154	0.102	0.017	0.003

Table 6: Amount of ions contributed in ion pairs for the study water samples

Locations	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>
Mzahmad	0.106	0.050	0.003	0.000	0.086	0.073
Qoritan 1	0.084	0.091	0.000	0.006	0.026	0.155
Qoritan 2	0.058	0.026	0.001	0.000	0.067	0.018
Pirdawd 1	0.191	0.118	0.005	0.000	0.098	0.216
Pirdawd 2	0.155	0.098	0.004	0.000	0.125	0.132
Quchabilbas 1	0.086	0.040	0.001	0.000	0.085	0.042
Haje Aleawa	0.219	0.097	0.003	0.000	0.085	0.234
Daldghan	0.167	0.111	0.004	0.000	0.134	0.148
Cheman	0.224	0.210	0.009	0.000	0.113	0.330



Chaltwk	0.241	0.216	0.027	0.000	0.126	0.358
Alla	0.227	0.224	0.015	0.000	0.136	0.330
Mastawa Shekhan	0.637	0.190	0.022	0.000	0.276	0.573
Kandarakal	0.391	0.371	0.060	0.001	0.188	0.635
Qara chnagha	0.065	0.029	0.005	0.000	0.029	0.070
Yadaqzlar 1	0.375	0.389	0.008	0.001	0.115	0.658
Yadaqzlar 2	0.293	0.392	0.010	0.000	0.156	0.539
Gabalak	1.538	1.596	0.094	0.002	0.147	3.083
Grdachal 1	4.037	3.520	0.418	0.017	0.198	7.794
Grdachal 2	3.389	3.002	0.492	0.007	0.176	6.714
Abo Sheta	0.414	0.307	0.015	0.000	0.133	0.603
Zaga	0.032	0.028	0.000	0.000	0.009	0.051
Qadria	0.059	0.043	0.002	0.000	0.024	0.080
Hawera	0.689	0.892	0.024	0.000	0.400	1.205
Klaw Rash	0.512	0.248	0.035	0.000	0.135	0.660
Kapran	0.377	0.290	0.021	0.000	0.127	0.561
Alyawa	1.012	0.830	0.004	0.000	0.793	1.053
Karasur 1	1.869	1.566	0.116	0.000	0.835	2.716
Karasur 2	2.690	1.636	0.136	0.001	1.332	3.131
Kalshkhan	1.420	1.464	0.136	0.001	0.780	2.241
Mehedi	2.293	2.277	0.110	0.001	1.232	3.449
Kndal	2.351	1.786	0.180	0.002	1.207	3.112
Sargran	1.585	1.264	0.102	0.001	0.744	2.208
Qushtapa	0.156	0.107	0.004	0.000	0.045	0.222
Murtakagawra	0.088	0.074	0.001	0.000	0.041	0.122
Sablagh	0.094	0.085	0.000	0.000	0.033	0.146
Quchabilbas 2	0.090	0.111	0.000	0.000	0.024	0.177
Mean	0.784	0.661	0.057	0.001	0.285	1.218
SD	1.033	0.893	0.110	0.003	0.374	1.823

Table 7 shows the range and mean of chemical properties of soil samples before and after correcting for ion pairs and activity, as determined from Table 2.

Table 7: Explain the influence of correcting ions and activity on soil chemical properties

Chemical properties	unit	range Before correcting ion pairs	mean $\pm$ SD	range After correcting ion pairs and activity	mean $\pm$ SD	activity coefficient
EC	dS m <sup>-1</sup>	0.41 - 5.19	2.69 $\pm$ 1.88	0.41 - 5.19	2.69 $\pm$ 1.88	
pH		7.19 - 8.10	7.58 $\pm$ 0.22	7.19 - 8.10	7.58 $\pm$ 0.22	
Ca <sup>+2</sup>		0.39 - 62.00	27.52 $\pm$ 26.22	0.24 - 16.14	8.32 $\pm$ 6.56	0.42
Mg <sup>+2</sup>		0.25 - 7.70	4.03 $\pm$ 2.49	0.16 - 3.10	1.59 $\pm$ 0.90	0.45
Na <sup>+</sup>		0.21 - 3.31	0.99 $\pm$ 0.98	0.16 - 2.95	0.85 $\pm$ 0.88	0.84
K <sup>+</sup>	mmolc L <sup>-1</sup>	0.09 - 0.86	0.31 $\pm$ 0.21	0.07 - 0.67	0.25 $\pm$ 0.16	0.82
CO <sub>3</sub> <sup>-2</sup>		N. D	N. D	N. D	N. D	N.D*
HCO <sub>3</sub> <sup>-</sup>		0.15 - 3.60	2.31 $\pm$ 1.24	0.14 - 2.81	1.76 $\pm$ 0.90	0.80

SO <sub>4</sub> <sup>2-</sup>	4.10 - 65.73	28.30 ± 26.52	2.02 - 14.88	7.66 ± 5.40	0.39
Cl <sup>-</sup>	0.28 - 2.60	1.41 ± 0.73	0.28 - 2.60	1.41 ± 0.73	Activity coefficient = activity/concentration

\*= Not detected

Table (8) explains that the amount of ion pairs in gypsiferous soil is higher than their amount in calcareous soil. This may be due to higher concentration of ions, especially Ca<sup>+2</sup> and SO<sub>4</sub><sup>-2</sup> in gypsiferous soils in addition to its high ionic strength, which ranged between 0.011 - 0.087 mole L<sup>-1</sup>. While in calcareous soil, the range was between 0.006 - 0.048 mole L<sup>-1</sup> and the ratio between ionic activity of gypsiferous to calcareous soil was 1.93, this may be due to the higher solubility of gypsum (2 g L<sup>-1</sup>) and low solubility of calcium carbonate 0.013 g L<sup>-1</sup>. It means the solubility of gypsum is 200 times higher than the solubility of calcium carbonate, which caused an increase in the concentration of Ca<sup>+2</sup> and SO<sub>4</sub><sup>-2</sup> in gypsiferous soil, then forming a higher amount of ion pairs, especially (CaSO<sub>4</sub>)<sup>0</sup> [13].

On the other hand, the ratio between ion pairs in gypsiferous to calcareous soil ranged from 0.67 to 3.19; the highest ratio was for (CaSO<sub>4</sub>)<sup>0</sup>, while the lowest ratios were for (MgHCO<sub>3</sub>)<sup>0</sup> and (NaHCO<sub>3</sub>)<sup>0</sup>. It appears that chemical composition and ionic strength had a great effect on the type of ion pairs; for example, the dominant ion pair in gypsiferous soil is (CaSO<sub>4</sub>)<sup>0</sup>, which ranged between (0.24 - 11.39) mmol L<sup>-1</sup>, which was recorded at Berabat and Ain-Talawi 1 locations. The series of ion pairs for both gypsiferous and calcareous soils were arranged as follow: ((CaSO<sub>4</sub>)<sup>0</sup>, (MgSO<sub>4</sub>)<sup>0</sup>, (CaHCO<sub>3</sub>)<sup>+</sup>, (MgHCO<sub>3</sub>)<sup>+</sup>, (NaSO<sub>4</sub>)<sup>-</sup>, (KSO<sub>4</sub>)<sup>-</sup>, and (NaHCO<sub>3</sub>)<sup>0</sup>) with the mean concentration of (6.35, 0.68, 0.20, 0.02, 0.01, 0.009 and 0.0004) mmol L<sup>-1</sup> respectively for gypsiferous soil. At the same time, their concentrations in calcareous soil were (1.99, 0.33, 0.12, 0.03, 0.008, 0.009, and 0.0006) mmol L<sup>-1</sup>, respectively. Furthermore, the ratio between the above ion pairs in gypsiferous to calcareous soils were (3.19, 2.06, 1.67, 0.67, 1.25, 1.00, and 0.67), which means that the mean of most ion pair in gypsiferous soil is higher than calcareous soil [14] This may be due to differing in the chemical composition of the mentioned two soils which caused differing in concentration of ions contributed in ion pairing (Table 9).

Table 8: Influence of soil type on concentration and types of ion pairs

Sampling Sites	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>
Ain-Talawi 1	11.67	1.39	0.03	0.01	0.32	12.80
Ain-Talawi 2	11.18	0.92	0.01	0.01	0.40	11.72
Sinu 1	11.72	1.44	0.02	0.01	0.39	12.81
Sinu 2	10.21	0.74	0.004	0.01	0.36	10.61
Makhmour	0.27	0.08	0.03	0.01	0.01	0.37
Jana	0.52	0.18	0.003	0.004	0.03	0.68
Berabat	0.26	0.15	0.002	0.002	0.07	0.38
Hamam Alil	5.00	0.29	0.003	0.01	0.21	5.09
Akre	0.03	0.02	0.01	0.001	0.001	0.07
Talkef	0.40	0.28	0.003	0.002	0.14	0.54
Alhamdania	0.53	0.35	0.004	0.001	0.15	0.73
Talul al baj	4.57	0.89	0.02	0.03	0.24	5.26

In general the correlation coefficient values between ion pairs ((CaSO<sub>4</sub>)<sup>0</sup>, (MgSO<sub>4</sub>)<sup>0</sup>, (CaHCO<sub>3</sub>)<sup>+</sup>, (MgHCO<sub>3</sub>)<sup>+</sup>, (NaSO<sub>4</sub>)<sup>-</sup>, (KSO<sub>4</sub>)<sup>-</sup>, and (NaHCO<sub>3</sub>)<sup>0</sup>) and ionic strength in gypsiferous soil were (r= 0.99\*\*, 0.98\*\*, 0.94\*\*, 0.93\*\*, 0.26<sup>n.s</sup>, 0.02<sup>n.s</sup>, and 0.87\*\*) respectively as shown from figures (6a to 6g). On the other hand, their values in calcareous soil were (r= 0.98\*\*, 0.98\*\*, 0.75\*\*, 0.087<sup>n.s</sup>, 0.11<sup>n.s</sup>, 0.014<sup>n.s</sup>, and 0.88\*\*) respectively as explained from figures (7a to 7g). It means the correlation between ion strength and ion pairs in gypsiferous soil higher than calcareous soil due to the reasons mentioned by [14] and [7].

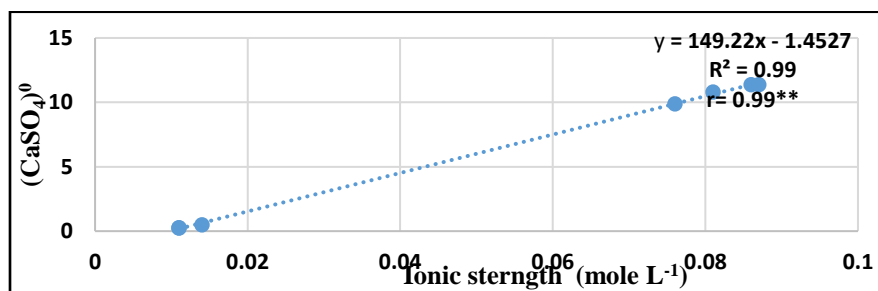


Figure 6a: Correlation between  $(\text{CaSO}_4)^0$  and ion strength in gypsiferous soil

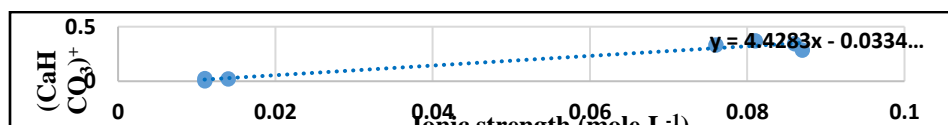


Figure 6b: Correlation between  $(\text{CaHCO}_3)^+$  and ion strength in gypsiferous soil

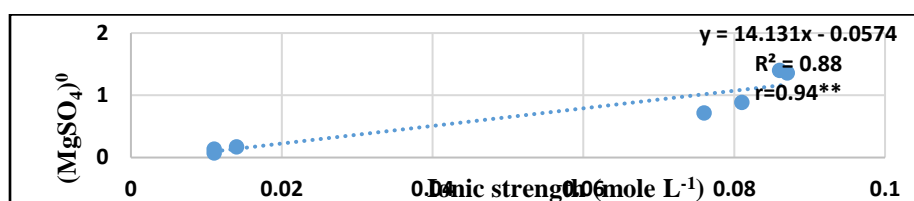


Figure 6c: Correlation between  $(\text{MgSO}_4)^0$  and ion strength in gypsiferous soil

Table (9) explains the amount of ions that contributed in ion pairs. The dominant ions that contributed in ion pairs are  $\text{Ca}^{+2}$  and  $\text{SO}_4^{-2}$ . The highest values of both  $\text{SO}_4^{-2}$  and  $\text{Ca}^{+2}$  was recorded from Sinu 1, which were equal to 11.72 and 12.81 and  $\text{mmol L}^{-1}$ , respectively, while the lowest values were recorded in Akre for both ions, which are equal to 0.03 and 0.07 and  $\text{mmol L}^{-1}$ , respectively.

Locations	Soil type	$(\text{CaSO}_4)^0$ $\text{mmol L}^{-1}$	$(\text{CaHCO}_3)^+$ $\text{mmol L}^{-1}$	$(\text{MgSO}_4)^0$ $\text{mmol L}^{-1}$	$(\text{MgHCO}_3)^+$ $\text{mmol L}^{-1}$	$(\text{NaSO}_4)^-$ $\text{mmol L}^{-1}$	$(\text{NaHCO}_3)^0$ $\text{mmol L}^{-1}$	$(\text{KSO}_4)^-$ $\text{mmol L}^{-1}$	Ionic strength $\text{mole L}^{-1}$
Ain-Talawi 1	Gypsiferous Soil	11.39	0.29	1.36	0.03	0.03	0.001	0.0120	0.087
Ain-Talawi 2		10.81	0.37	0.89	0.03	0.01	0.000	0.0130	0.081
Sinu 1		11.38	0.35	1.40	0.04	0.02	0.001	0.0100	0.086
Sinu 2		9.88	0.33	0.72	0.02	0.004	0.000	0.0110	0.076
Makhmour		0.26	0.01	0.08	0.001	0.03	0.001	0.0080	0.011
Jana		0.50	0.02	0.18	0.01	0.003	0.000	0.0040	0.014
Berabat		0.24	0.02	0.14	0.01	0.002	0.000	0.0020	0.011
Mean		6.35	0.20	0.68	0.02	0.01	0.0004	0.009	0.052
Hamam Alil		4.80	0.20	0.28	0.01	0.003	0.000	0.0130	0.047
Akre		0.03	0.0003	0.02	0.0002	0.014	0.0001	0.0010	0.006
Talkef	Calcareous Soil	0.31	0.08	0.23	0.05	0.002	0.001	0.0020	0.015
Alhamdania		0.44	0.09	0.29	0.06	0.003	0.001	0.0010	0.018
Talul albaj		4.37	0.21	0.85	0.04	0.016	0.001	0.0270	0.048
Mean		1.99	0.12	0.33	0.03	0.008	0.0006	0.009	0.027
Ratio		3.19	1.67	2.06	0.67	1.25	0.67	1.00	1.93

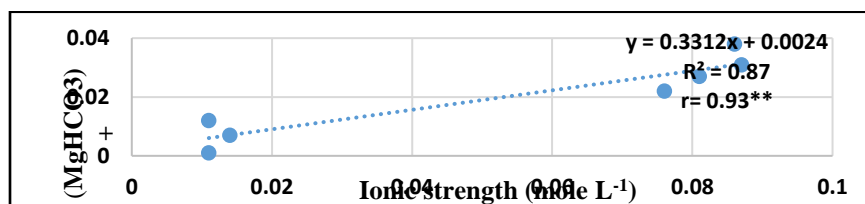


Figure 6d: Correlation between  $(\text{MgHCO}_3)^+$  and ion strength in gypsiferous soil

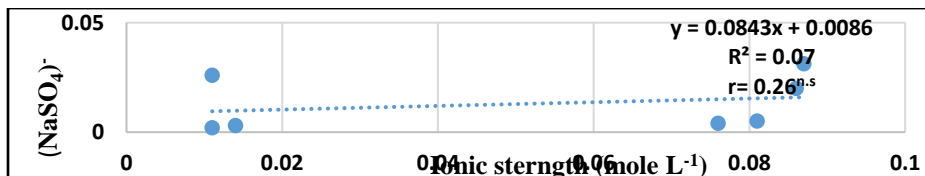


Figure 6e: Correlation between  $(\text{NaSO}_4)^-$  and ion strength in gypsiferous soil



Figure 6f: Correlation between  $(\text{NaHCO}_3)^0$  and ion strength in gypsiferous soil

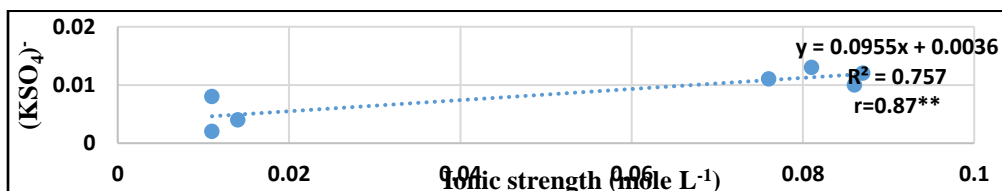


Figure 6g: Correlation between  $(\text{KSO}_4)^-$  and ion strength in gypsiferous soil

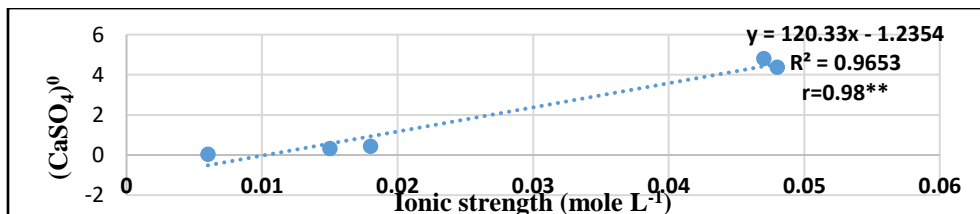


Figure 7a: Correlation between  $(\text{CaSO}_4)^0$  and ion strength in calcareous soil

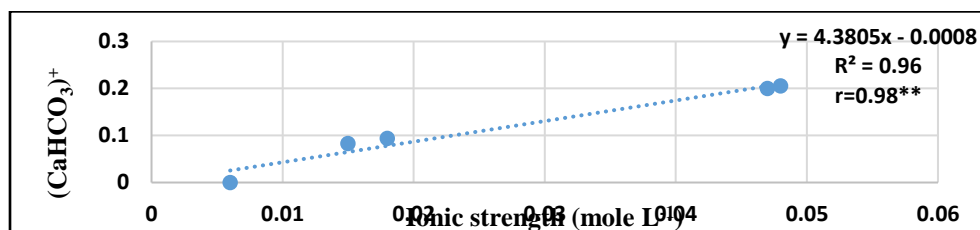


Figure 7b: Correlation between  $(\text{CaHCO}_3)^+$  and ion strength in calcareous soil

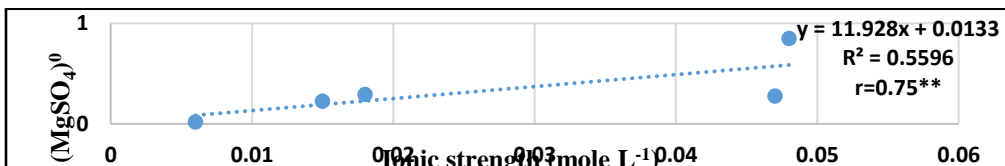


Figure 7c: Correlation between  $(\text{MgSO}_4)^0$  and ion strength in calcareous soil

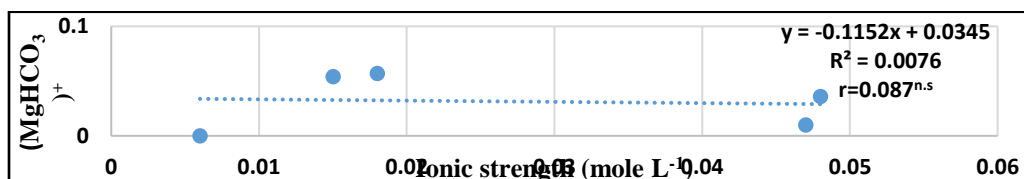


Figure 7d: Correlation between  $(\text{MgHCO}_3)^+$  and ion strength in calcareous soil

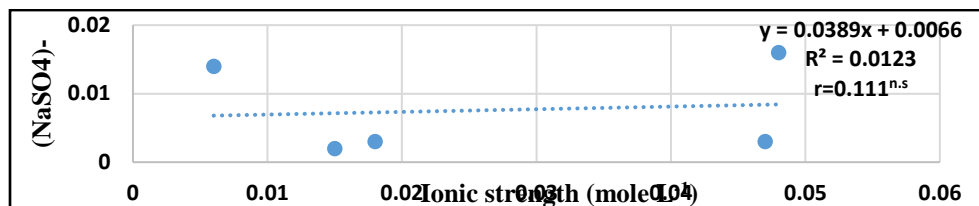


Figure 7e: Correlation between  $(\text{NaSO}_4)^+$  and ion strength in calcareous soil

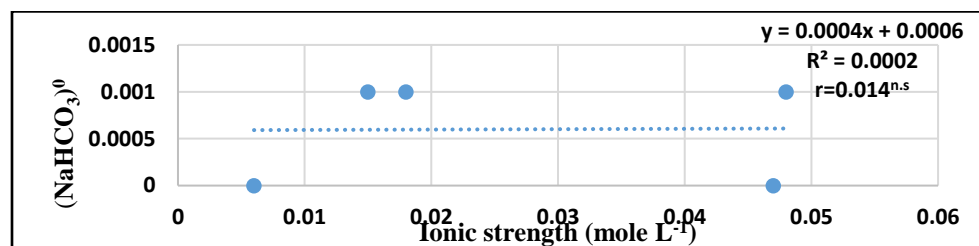


Figure 7f: Correlation between  $(\text{NaHCO}_3)^0$  and ion strength in calcareous soil

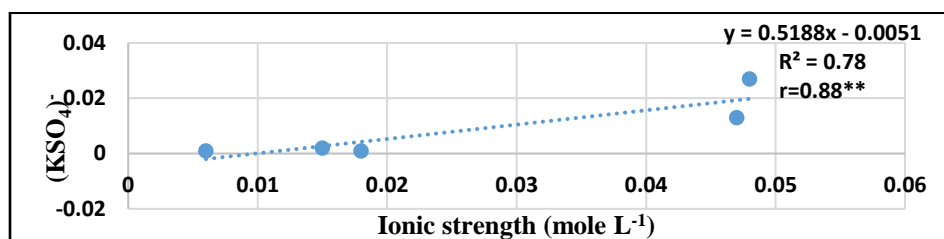


Figure 7g: Correlation between  $(\text{KSO}_4)^-$  and ion strength in calcareous soil

## Conclusion

The amount and type of ion pairs were affected by water and soil types. The highest values of ion pairs were recorded from Ca-SO<sub>4</sub> water type and gypsiferous soil. The chemical composition of water and soil affected the amount of ion pairs and the amount of ions contributing to ion pairing. These results impact water management since the increase in the amount of ion pairs causes a decrease in the risk of using saline water for irrigation. Ion pairs cannot contribute to chemical reactions and are not absorbed by plants, which also causes a decrease in their risks to plants.

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## كيمياء المياه ونوعية التربة كعوامل رئيسية في تكوين الأزودواج الأيوني.

كاثرين سرباز رجب

قسم التربة والمياه، كلية هندسة العلوم الزراعية، جامعة صلاح الدين، أربيل، العراق

### الخلاصة

أخذت عينات مياه الجوفية من 36 بئرا في أربيل وضمت عينات ترب كلسية وجبسية، من مواقع مختلفة في محافظتي أربيل ونيوى. وقد حلت بعض الخصائص الكيميائية للمياه والتربة المدروسة. ثم حددت أنواع المياه والتربة، وحسبت الأيونات المزدوجة والفعالية الأيونية، وقوة الأيونية. وكانت النتائج الرئيسية كما يلي: كانت نوعية المياه لـ (11، 10، 9، 2، 2، 2) بئرا قبل تصحيح الأزودواج الأيوني ضمن نوعية ( $Ca-SO_4$ ،  $Ca-HCO_3$ ،  $Mg-SO_4$ ،  $Mg-HCO_3$ ،  $Na-HCO_3$ ،  $Na-SO_4$ ) على التوالي. أما بعد تصحيح الأزودواج الأيوني والفعالية الأيونية سجلت مياه لـ (1، 16، 3، 6، 7، 3) بئرا نوعيات السابقة الذكر على التوالي، أي أثرت تصحيح الأزودواج الأيوني إلى تغير كبير في نوعية المياه من نوع إلى آخر بشكل كبير. تمثل عينات التربة سبع ترب جبسية وخمس ترب كلسية، اعتمادا على محتواها من كربونات الكالسيوم والجبس. كمية الأيونات المزدوجة في التربة الجبسية أعلى منها في التربة الكلسية. تراوحت النسبة بين الأيونات المزدوجة في التربة الجبسية والكلسية بين 0.67 و 3.19، وأعلى قيمة هي للـ ( $CaSO_4$ ) بينما أدنى قيمة هي للـ ( $MgHCO_3$ ). تم ترتيب سلسلة الأيونات المزدوجة لكلا التربة الجبسية و كلسية كالتالي ( $CaSO_4$ )<sup>o</sup>، ( $MgSO_4$ )<sup>o</sup>، ( $CaHCO_3$ )<sup>+</sup>، ( $MgHCO_3$ )<sup>+</sup>، ( $NaSO_4$ )<sup>-</sup>، ( $KSO_4$ )<sup>-</sup>، و ( $NaHCO_3$ )<sup>o</sup>. الأيونات السائدة المساهمة في تكوين الأيونات المزدوجة هي  $Ca^{+2}$  و  $SO_4^{-2}$ ، وقد سجلت أعلى القيم لهما في تربة *Sinu1*، بينما أدنى القيم سجلت في تربة *Akre* لكلا الأيونين. سجلت أعلى قيمة لمعامل الارتباط بين قوة الأيونية والأيونات المزدوجة في التربة الجبسية مقارنة بالتربة الكلسية حيث بلغت معدل معامل الارتباط لهما ( $r^{**} = 0.71$  و  $0.54$ )، على التوالي.

الكلمات المفتاحية: التركيب الكيميائي للمياه، المياه الجوفية، القوة الأيونية، التربة الكلسية، التربة الجبسية.