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HYDROCHEMICAL SITUATION OF SHARI PLAYA LAKE BRINES AND THE CONTRIBUTION OF THE FEEDING WATER TO THE FORMATION OF EVAPORITE MINERALS, CENTRAL IRAQ

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Key words: Hydrochemistry, Sodium sulphate, Glauberite, Thenardite, Shari Playa, Iraq

ABSTRACT

Shari Playa is a closed elongated basin about 20 Km long and (3 – 5) Km wide; located about 150 Km north of Baghdad. It is characterized by the presence of a lake in winter which dries out to form salt playa in summer. The lake water concentrates by evaporation to form salt crust; composed of sodium chloride and sodium sulphate. Since the playa is a structural depression, many springs are developed inside it as a result of faults intersections. The water and brines in the Shari Playa basin indicate three major groups of water: $Na^+ – Cl^- – SO_4^=$; $Ca^{2+} – SO_4^=$ and $Na^+ – Ca^{2+} – SO_4^=$. Where the second cations and anions concentrations vary in different water sources in Shari Playa basin, other subdivisions may be recognized giving different water types. The supplied water to the depression strongly contributes to the formation of glauberite, gypsum and thenardite in the lake sediments, especially in the central part which is characterized by the presence of organic matter in the sediments. The water and brines are of different hydrochemical characteristics and contributes to the formation of different evaporite minerals or to dissolve them depending on their concentrations. The lake water precipitates gypsum at first, then glauberite forms in the deepest part of the playa lake when the water volume decreases to occupy the central part only. The concentration of the remaining brine increases due to evaporation, where Na^+ is high enough to alter gypsum to glauberite [$Na_2Ca(SO_4)_2$]. Thenardite (Na_2SO_4) forms in the salt crust when all Ca^{2+} is consumed from the lake brine before the NaCl precipitation. It also forms within the black mud slurry after ending of glauberite formation, which consumes the Ca^{2+} in the brine.

الوضع الهيدروكيميائي لمنخفض الشاري والمياه المغذية لها ومساهمتها في تكون المعادن الملحية، وسط العراق

رافع زائر جاسم و يحيى توفيق الراوي و حبيب رشيد حبيب

المستخلص

منخفض الشاري حوض شبه مغلق يبلغ طوله حوالي 20 كم وعرضه يتراوح بين (3 – 5) كم ويقع علي بعد 150 كم شمال بغداد. يتصف هذا المنخفض بتكون بحيرة في الشتاء، سرعان ما تجف في الصيف مكونةً منخفض ملحي. تتركز مياه البحيرة بالتبخير مخلفةً قشرة ملحية تتألف من كلوريد الصوديوم وكبريتات الصوديوم. وحيث أن المنخفض ذو أصل تركيبي، فإن العديد من العيون قد تكونت داخل

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المنخفض نتيجة تقاطع الصدوع ذات الإتجاهات المختلفة. تظهر الدراسة أن هناك ثلاثة أنواع رئيسية من المياه وهي: $Na^+ - Cl^- - SO_4^=$ و $Ca^{2+} - SO_4^=$ و $Na^+ - Ca^{2+} - SO_4^=$ وضمن هذه المجاميع الرئيسية توجد تقسيمات ثانوية أخرى نتيجة تغاير تواجد الأيونات الموجبة والسالبة من مصدر إلى آخر من هذه المياه. تعتبر المياه التي يتزود بها المنخفض مسؤولة بشكل كبير عن تكون معادن الگلوبرايت والجبسم والثنردايت في رسوبياته وخصوصاً في الجزء المركزي منه والذي يتصف بوجود المواد العضوية ضمن الطبقة الطينية السوداء خفيفة القوام، حيث إن هذه المياه أو المحاليل ذات صفات جيوكيميائية مختلفة وتراكيز مختلفة قد يؤدي بعضها الى ترسيب معدن معين والبعض الآخر إلى معدن آخر أو قد يساهم في إذابة المعادن الملحية المترسبة. يترسب معدن الجبس من مياه البحيرة أولاً، ثم يتبعها ترسب معدن الگلوبرايت في المنطقة العميقة من البحيرة، حينما تتقلص مياه البحيرة لتغطي الجزء المركزي منها. في هذه المرحلة يزداد تركيز محاليل البحيرة نتيجة التبخير بحيث إن تركيز أيون الصوديوم يكون كافياً لتحويل الجبسم الى گلوبرايت. $[Na_2Ca(SO_4)_2]$ يترسب معدن الثنردايت (Na_2SO_4) في القشرة الملحية بعد أن يستهلك كل تركيز أيون الكالسيوم من المحاليل قبيل ترسيب كلوريد الصوديوم. يتكون الثنردايت أيضاً في الطبقة الطينية السوداء بعد اكتمال تكون الگلوبرايت الذي يستهلك أيون الكالسيوم من محاليل هذه الطبقة.

INTRODUCTION

The Shari Playa is located about 150 Km north of Baghdad. It has been considered as a graben affected by three sets of faults (Jassim *et al*., 2006). The hydrochemistry of the incoming water and brines to a closed basin largely control the final composition of the ponded brine in the basin. The hydrochemical characteristics of the brines depend on the abundance of major cations and anions of the water flowing into this closed basin. These ions are provided by runoff water, which is basically rainwater, washing out the soil and loose sediments in the catchment area. The ascending groundwater through weakness zones, springs and seepages carry out solutes dissolved from the sediments of the underlying formations.

The unique salt minerals assemblage of Shari Playa deposits among the other Iraqi salt lakes, playas and sabkhas, drew the attention of many workers to study its geology and economic potential. The previous works on Shari Playa and the surrounding area are arranged in chronological order, and briefed hereinafter.

- Parsons (1955) studied the groundwater quality and sources.
- Bolton (1956) studied the geology, geomorphology and economic potential of Shari Lake and the adjacent area.
- Al-Rawi (1970) studied the quality and amount of NaCl salt produced by the salters from the lake.
- El-Kiki *et al*. (1974) studied the hydrogeology and hydrochemistry of Mukdadiya Formation (Lower Bakhtiari) aquifer for the area surrounding Shari Lake.
- Araim *et al*. (1976) studied the hydrochemistry of the lake brine, hydrological properties of Lower Bakhtiari (Mukdadiya Formation) aquifer, geologic history and economic potential of the lake.
- Jajjoo *et al*. (1976) studied the possibilities of separation of sodium sulphate in the laboratory.
- Duffek (1977) gave brief description of the lake and its hydrochemistry and suggestions of brine utilization to produce chloride and sulphate salts.
- Yahya (1977) studied the annual fluctuation of water level in Shari Lake.
- Araim *et al*. (1978) studied the economic evaluation of the lake and sodium sulphate and chloride reserve estimation.

- GEOSURV (1978) carried local extraction and separation of sodium chloride and sulphate. Failure of this large scale experiment is due to the crystallization of all salts in the same basin and the difficulty of collecting salt brines in summer.
- Al-Kadhimi and Al-Attar (1982) carried out gravity geophysical survey and showed that most structures are directed NW-SE and the faults are either parallel or perpendicular to them.
- Yelda (1989) studied the genesis and geochemistry of some salt deposits in Iraq.
- Jassim (1989) studied the hydrochemistry of lake brines and summer and winter salt minerals deposited in the lake with their limitations for precipitations.
- Shakir (1989) supervised drilling of two boreholes of 68.7 m and 81.0 m in depth drilled at the eastern side of Shari Playa. Hydrochemistry of the groundwater from Mukdadiya Formation (Lower Bakhtiari) was also studied.
- Fatih (1989) studied the hydrochemistry of the lake brines and the chemistry and mineralogy of the uppermost sediments of the lake.
- Al-Kadhimi and Ahmed (1991) gravity, magnetic, seismic and geoelectric work for the area surrounding Samarra – Dour, which throw light on the structural and tectonic characteristics of the basement and sedimentary cover.
- Jassim (1992) studied the chemistry, mineralogy and economic evaluation of the lake sediments by drilling ten boreholes inside the lake. Sodium sulphate reserve was also estimated. A technological route for sodium sulphate extraction from the lake sediments, were suggested.
- Habib *et al*. (1992) studied the separation of sodium sulphate from the brines and water of Shari Lake.
- Al-Obaidi *et al*. (1992) carried out feasibility study and outlined the material balance, technology and feasibility of sodium sulphate extraction from the lake sediments.
- Mohammed and Jassim (1994) studied the mineralogy and possible genesis of salts.
- Al-Samarrai (1995) outlined the geomorphology of Shari Lake region using remote sensing techniques.
- Ahmid and Murad (1995) reported on water wells drilled for sodium sulphate plant nearby the Shari Lake.
- Jassim *et al*. (1997) studied the role bacteria in Shari Playa and their pathogenic effect.
- Jassim (1997) studied the sedimentology, structure, origin, mineralogy, geochemistry and hydrochemistry of Shari Playa.

GEOLOGY OF THE STUDIED AREA

Since the surface water brought to Shari Playa is affected by the rocks and sediments of the catchment area, it is necessary to throw light on the geology of the playa surroundings. Most of the water volume descends to Shari Playa come from Himreen Mountain, where the oldest formations from Shari Playa sediments, are exposed (Fig.1).

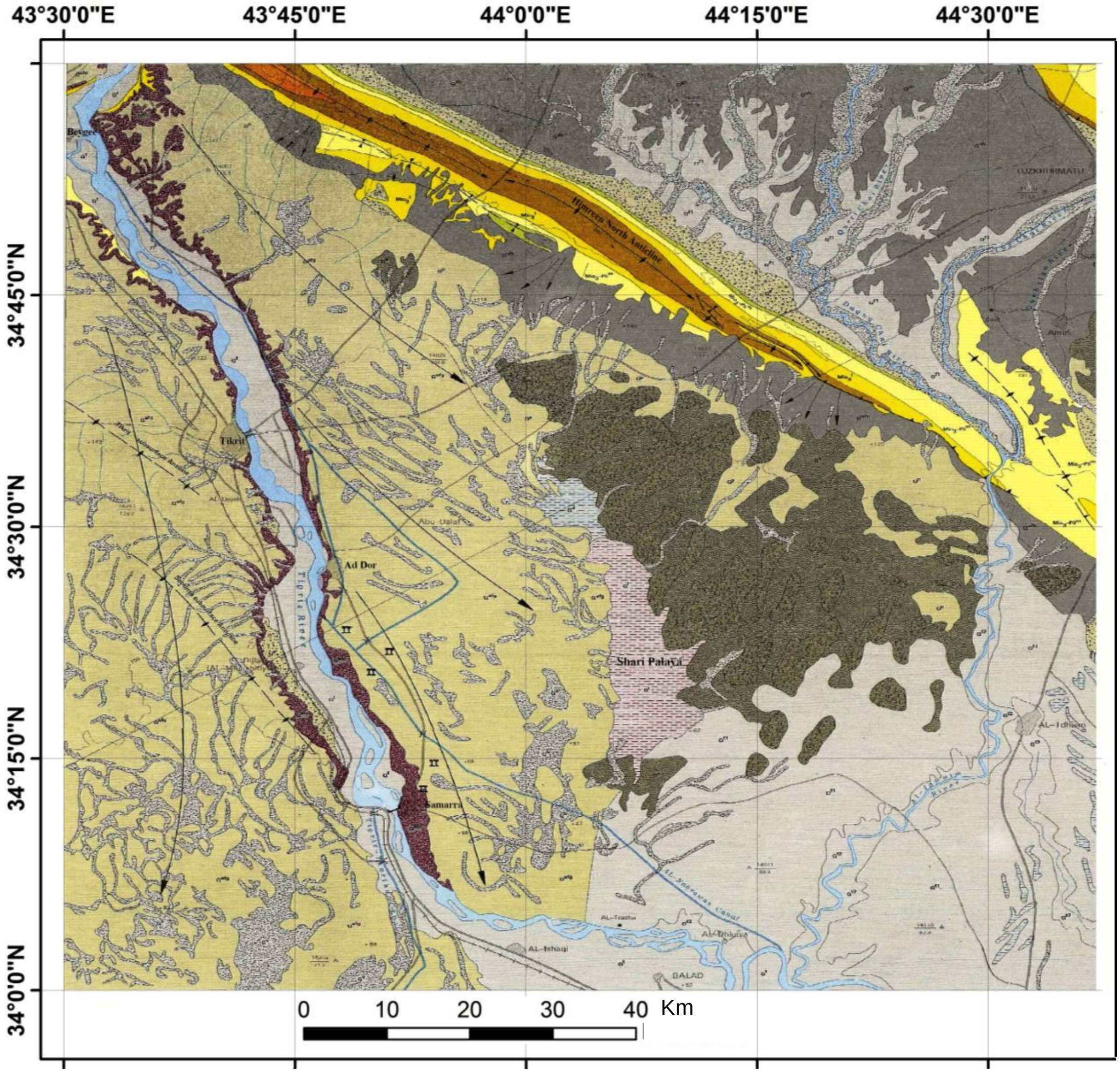
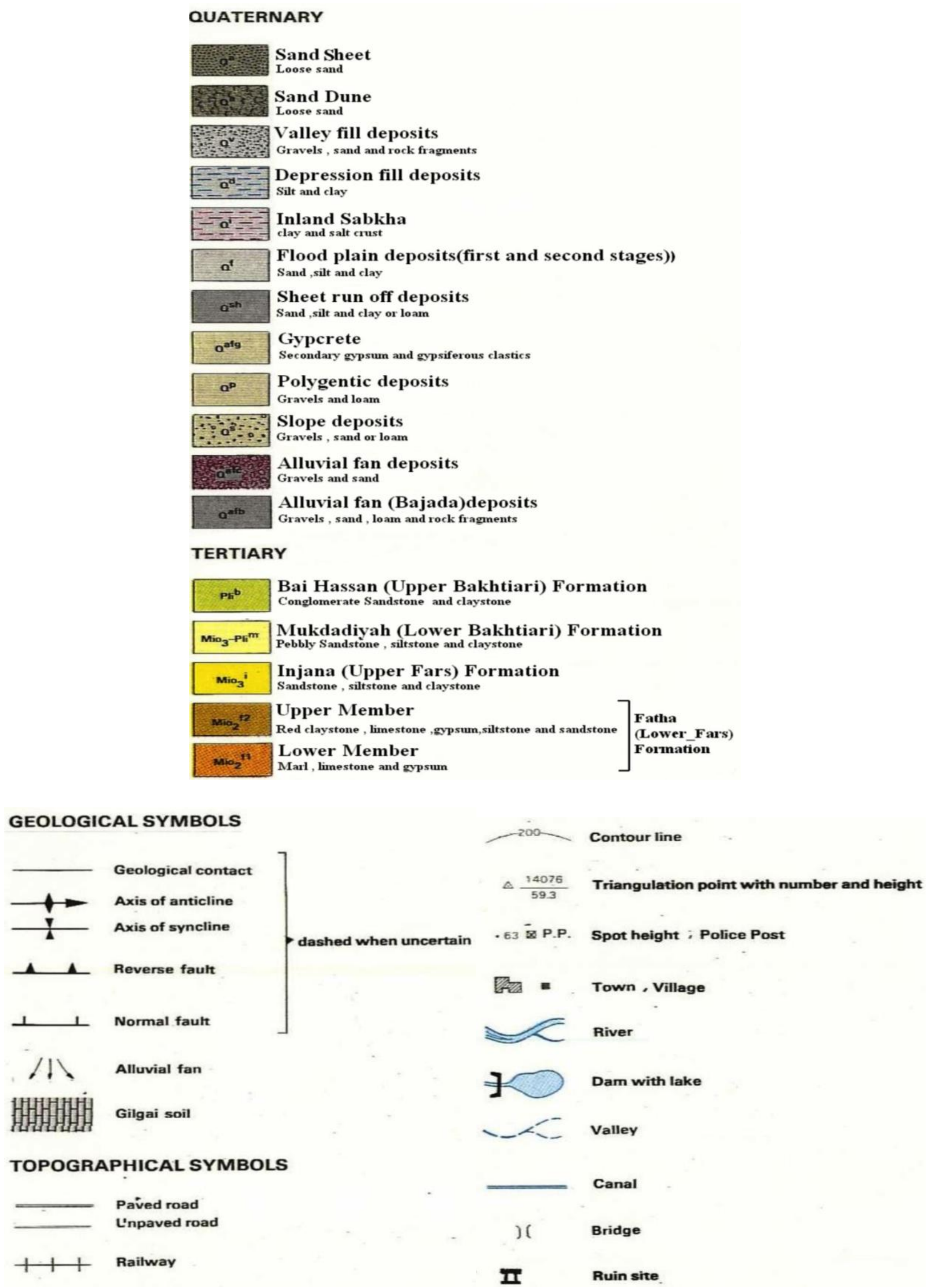


Fig.1: Location map of Shari Playa (after Sissakian and Fouad, 2012)



Continue Fig.1:

The geological formations exposed in the area surrounding the Shari Playa are Fatha (Middle Miocene), Injana (Late Miocene) and Mukdadiya (Late Miocene) formations as well as Quaternary sediments. Rock units of the Fatha and Injana formations are exposed in Himreen Mountain and extend beneath the playa area below the Quaternary sediments and Mukdadiya Formation. It has been found from the drilling data of Araim *et al*. (1976), Shakir (1989) and Ahmid and Murad (1995) at the western and eastern sides of the playa that the Mukdadiya Formation appears at depth ranging between (40 and 60) meters. The Mukdadiya Formation is composed of pebbly sandstone alternation with sandstone and mudstone layers (Buday, 1980 and Jassim and Goff, 2006). It is overlain by the Pleistocene fluvial sediments, which are composed of sand, silt and clay alternations. The Pleistocene sediments are considered as the substrata for the overlying playa sediments and saline deposits. While at the eastern and northern sides of the playa is occupied by the sand dune fields (Fig.2).

Jassim *et al*. (2006) suggested that the Shari playa was formed as graben and there are three fault systems intersecting in the playa, which are responsible for the springs present inside the playa depression.

SAMPLING AND METHOD OF WORK

Fifty three water and brine samples were collected representing the playa lake brines, water from the ephemeral streams, brines from the different playa facies and sub-environments, and Mukdadiya Formation's aquifer. The samples were collected during 1994 – 1995 and their sampling locations are presented in Fig. (2) and two playa lake brines were collected during winter 2013. Observations of Shari playa from 1995 to 2013 showed that during the dry years the lake is dry, whereas in the wet years it is covered with water, which indicate that the main source of the lake water is the rain water flowing to the playa depression through the ephemeral streams descended from the catchment area.

Chemical analyzes of fifty three water and brine samples were performed to characterize the Shari Playa system. Major and minor ions including sodium (Na^+) calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sulphate ($SO_4^=$), chloride (Cl^-), carbonate ($CO_3^=$) and bicarbonate (HCO_3^-), the results are presented in Table (1). The chemical analyzes were carried out in the laboratories of Iraq Geological Survey according to the Work Procedure Part 21 (Al-Janabi *et al*., 1993). These analyzes were utilized to determine the hydrochemical characteristics of the water and brines and to understand its role in the formation of the evaporite minerals precipitated in the playa.

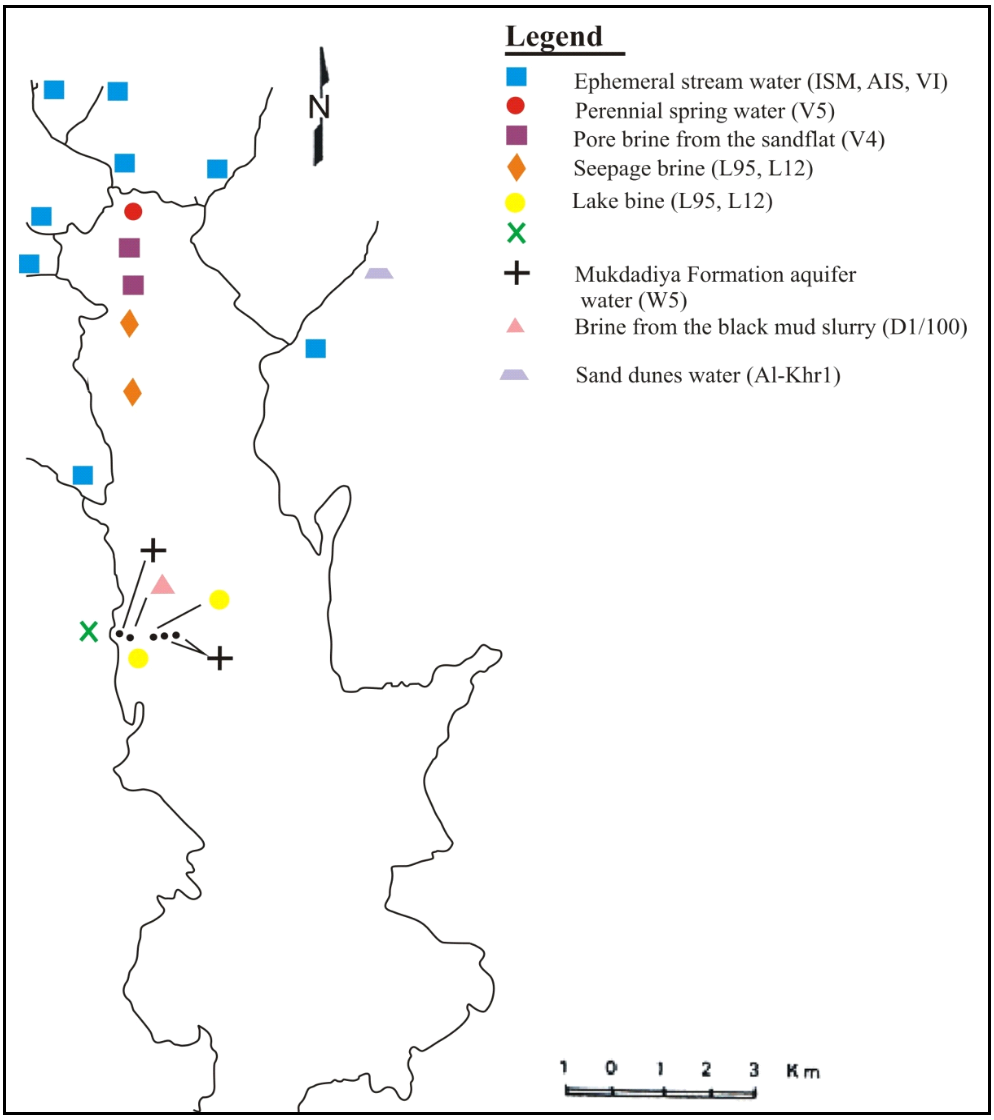


Fig.2: Location map of water samples from Shari Playa basin

RESULTS AND DISCUSSION

- **Classification of Hydrochemical Data**

Classification methods are used for hydrochemical characterization to differentiate the chemical types of water and brines and to identify the dominant type in the Shari playa basin. There are many methods to illustrate the results of the chemical analyzes; among these are Korlov formula and Piper's classification (Matthess, 1982). In Korlov formula, the anions and cations of the chemical analysis are expressed in the numerator and dominator, respectively as shown below:

T.D.S.	Anions in epm% in descending order (> 15 epm%)	pH
	Cations in epm% in descending order (> 15 epm%)	

The hydrochemical formula of the studied water and brine samples from the Shari Playa basin are given in Table (1). They are grouped in nine groups:

$Na^+ – Cl – SO_4^=$	Represented by: Playa lake brine, water from one of the western ephemeral streams, ephemeral stream on the eastern side and from the flood plain-alluvial fan sub-environment.
$Na^+ – SO_4^= – Cl^–$	Represented by: Western ephemeral streams water, water from well in the dune field and few playa lake brines.
$Na^+ – Cl^–$	Represented by: Pore brine from the glauberite-rich mud and seepages inside the playa.
$Na^+ – Mg^{2+} – SO_4^= – Cl^–$	Represented by: Edmath ephemeral stream at the northern end of the playa.
$Na^+ – Ca^{2+} – Mg^{2+} – SO_4^= – Cl^–$	Represented by: water of Mukdadiya Formation aquifer.
$Ca^{2+} – Mg^{2+} – SO_4^= – Cl^–$	Represented by: Water seeping from the sand dunes into Wadi Abu Al-Asuad.
$Ca^{2+} – SO_4^=$	Represented by: Water from a branch of Wadi Assam.
$Ca^{2+} – Na^+ – SO_4^=$	Represented by: Water from branch of Wadi Assam.
$Na^+ – Ca^{2+} – SO_4^=$	Represented by: Water from Wadi Assam, and the perennial spring water.

Two samples of the Playa lake brine were sampled at two different dates in winter of 2013 and were found to be $Na^+ – SO_4^= – Cl^–$ type.

The formula clarifies the characteristics of the water and brines in the Shari Playa basin and indicate three major groups of these water: $Na^+ – Cl^– – SO_4^=$; $Ca^{2+} – SO_4^=$ and $Na^+ – Ca^{2+} – SO_4^=$. Within these three major groups, other subdivisions may be recognized as the second cations and anions vary from place to other giving different types of water.

Among the methods of classifying water types is Piper classification (1944), which is also followed in this work (Figs.3 and 4). This classification is the most useful, as it comprises a genetic relation between the water types. The classification deals efficiently with the brines as well as water according to the dominant cations and anions (in epm%) to find differences or similarities in chemical composition. The distribution of the analyzes from the Shari playa in the diamond shaped field (Fig.3) indicates the following:

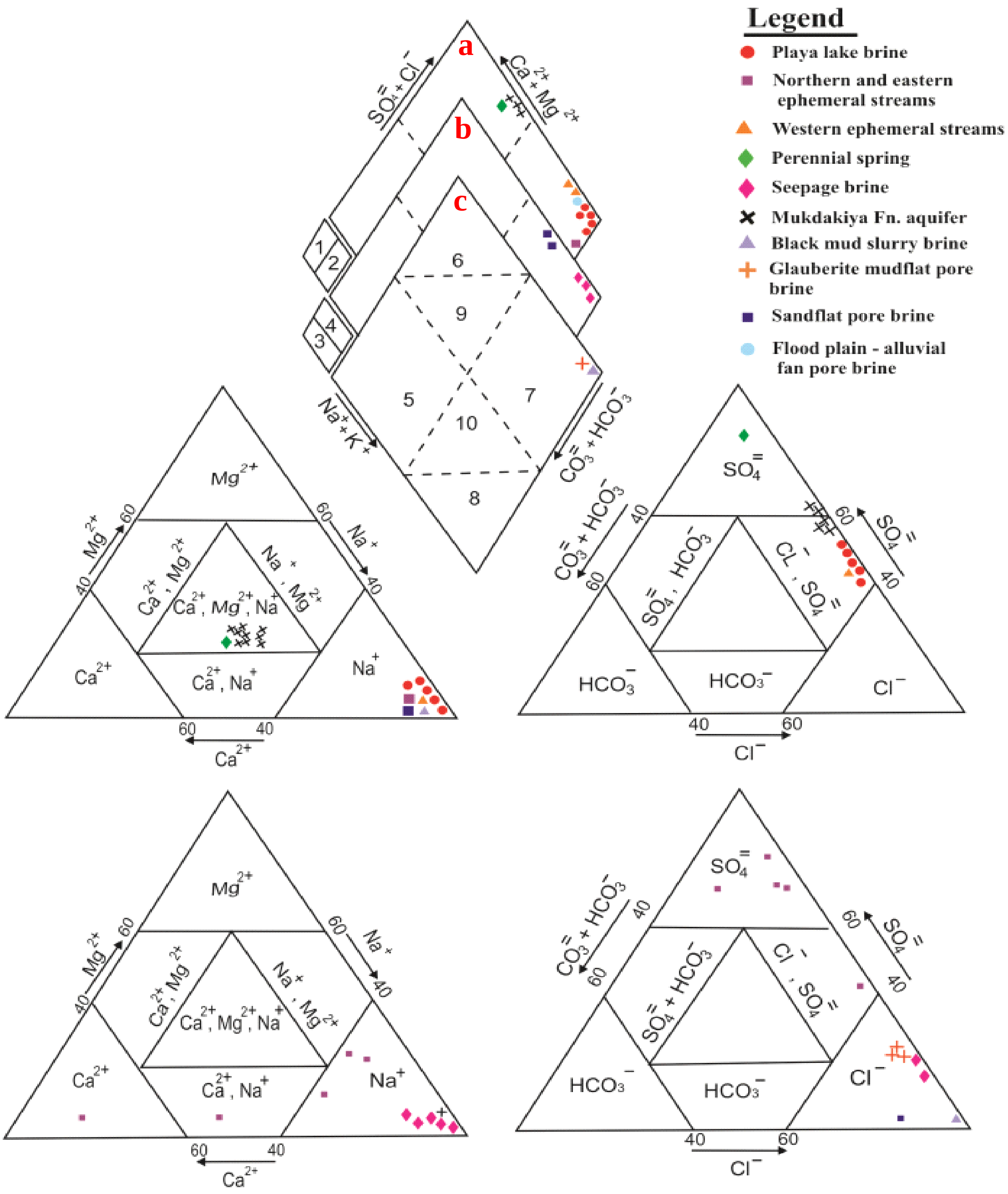


Fig.3: Hydrochemical results of water and brines from the Shari Playa basin plotted on Piper's triangles and diamond shape diagram

- The playa lake brine, water of the western ephemeral streams, brines of the sand flat sub-environment, brine of the flood plain – alluvial fan sub-environment, seepage brines, brine of the black mud slurry, brine of the glauberite mudflat sub-environment and the water of the northern ephemeral streams are located in the field No.7 (Fig.3a, b and c). This field is characterized by the dominance of the alkalis ($Na^+ + K^+$) over the alkaline earths ($Ca^{2+} + Mg^{2+}$), the strong acids ($Cl^- + SO_4^=$) over the weak acids ($HCO_3^- + CO_3^=$) and by a primary salinity (alkali salinity) of > 50%. The primary salinity is the salinity that does not exceed twice the sum of the alkali ions (Matthess, 1982).

- Closeness of the plots of the water of the western ephemeral streams and the brines from the flood plain – alluvial fan indicates that they are genetically related (Fig.3a, field 7). Water of the northern ephemeral streams also has similar relationship with the flood plain – alluvial fan brine (Fig.3b). Figure (3b and c) show that the seepages brines, glauberite-rich mud pore brine, the playa lake brine and the brine from the black mud slurry have genetic relationship. The brine from the sand flat is separated from the other brines and water; therefore, it is probably not related to the other types. The water from the Mukdadiya Formation and the perennial spring water are located in the field No.6 (Fig.3a). This field is characterized by the dominance of the alkaline earths (Ca^{2+} + Mg^{2+}) over the alkalis (Na^{+} + K^{+}), the strong acids (Cl^{-} + $SO_4^{=}$) over weak acids (HCO_3^{-} + $CO_3^{=}$) and by a secondary salinity of > 50%. The secondary salinity (non-carbonate hardness) is the excess of salinity over the primary salinity; it does not exceed twice the total of the alkaline earths (Matthess, 1982). It should be noted that the presence of more than one plot close to each other in the fields in the diamond shape (Fig.3) may indicate genetic relationships among these plots. In this sense, the presence of the samples from Mukdadiya Formation's aquifer close to that of the perennial spring indicates that Mukdadiya Formation's aquifer is the possible source for the perennial springs.

Plotting the concentration of the main cations and anions of water and brines from the Shari Playa basin, on Piper's diagram (Fig.3), shows that most water and brines fall into two cation facies. The playa lake brine, western ephemeral streams water, glauberite-rich mud pore brine, seepages brines, and water of some of the northern ephemeral streams show Na^{+} facies. Whereas the water from Mukdadiya Formation's aquifer and the perennial spring, show Na^{+} – Ca^{2+} – Mg^{2+} facies without dominant cation. On the other hand, the anion triangle shows that the seepages brines, glauberite-rich pore brine, the black mud slurry brine, and the playa lake brine have Cl^{-} facies. The Mukdadiya Formation's aquifer is of $SO_4^{=}$ – Cl^{-} facies, whereas the uppermost part of this aquifer and the perennial spring water are of $SO_4^{=}$ facies.

▪ Behavior of Hydrochemical Constituents

Concentrations of the major cations and anions of all water sources and brines in the Shari Playa basin are summarized in Table (1). All water and brines in the Shari Playa basin are weak alkaline with pH values ranging between 7.2 and 8.2, except for the western ephemeral streams, which have higher alkalinity (pH = 9.0).

The dissolved solids distribution in the Shari Playa basin is shown in Fig. (4). It shows an increase in concentration towards the basin center, i.e. the dissolved solids in the water of the ephemeral streams that recharge the playa are less than that of the playa lake brine and the pore sediments brine. Water samples from the boreholes drilled in the Mukdadiya Formation's aquifer (mixed with the water of the overlying sediments) as well as that of the perennial springs show low to intermediate T.D.S. The increment of T.D.S. concentration in the playa lake brine starts from the wet season to the dry season, reflecting the evolution of the brine with evaporation. The brines from the black mud slurry and the pore sediments show high to very high T.D.S. concentrations because they resemble the saturation stage due to evaporation near the surface.

The average of the major chemical constituents of different water and brines from the Shari Playa basin are shown in Table (1). The possible relations between these water and brines, in view of the hydrological/ hydrogeological cycle in the Shari Playa area are summarized in Table (2), which shows the compositional change in terms of enrichment and depletion of the constituent ions from one type of water (considered as a source) to another (considered as a resultant brine) and the possible precipitation of mineral phases that could produce such change.

The evolution of water of the ephemeral streams into the early and late playa lake brine results in the precipitation of Ca^{2+}, Mg^{2+} and $SO_4^{=}$ (precipitation of gypsum) and enrichment in Na^{+}, K^{+} and Cl^{-} in the remaining brine (Table 2), i.e. the lake brine is depleted in Ca^{2+}, Mg^{2+} and $SO_4^{=}$ and enriched in Na^{+}, K^{+} and $C1^{-}$ relative to the waterof the ephemeral streams. The ephemeral streams represent the lake's major water resource.

Comparing the composition of the early playa lake brine with the late lake brine may show the enrichment in Mg^{2+}, K^{+} and Cl^{-} and depletion in Ca^{2+} and $SO_4^{=}$ with negligible change in Na^{+} epm% (Table 2). Such a change may be affected by the precipitation of gypsum and to a lesser extent, thenardite and/ or glauberite in the playa lake sediments as the brine becomes more concentrated through evaporation.

Evolution of the playa lake brines into the underlying black mud slurry brine results in the enrichment in Mg^{2+} and Cl^{-} and depletion in Na^{+} and $SO_4^{=}$. This depletion could beaffected by the precipitation of glauberite and thenardite from the brine, as well as the conversion of pre-existing gypsum into glauberite (Table 2).

Similarly, evolution of the black mud slurry brine into the brine of the underlying glauberite-rich mud brine may result from the precipitation of halite (Table 2).

Evolution of the ephemeral streams water into the brine from the glauberite-rich mud, which shows an enrichment in Na^{+} and Cl^{-} and a depletion in Ca^{2+}, Mg^{2+}, K^{+} and $SO_4^{=}$ may result from the precipitation of gypsum. This may explain the gypsum enrichment in the sediments located between the ephemeral streams; on the peripheries of the playa and the glauberite-rich mud which is developed in the central part of the playa.

Upward migration of the ground water is also anticipated and may be considered here. The evolution of water from the Mukdadiya Formation's aquifer into the brine of the glauberite-rich mud as well as into the seepage brine at the surface of the playa may result from the precipitation of gypsum, which may explain the dominance of this phase in the sediments underlying this facies. Similarly, the evolution of the brine of the glauberite-rich mud into the brine of the overlying black mud slurry may be affected through further precipitation of gypsum; the paucity of gypsum in the glauberite-rich mud facies is probably due to its conversion into glauberite, because of the high concentration of Na^{+} in the brine. Therefore, the groundwater movement from the aquifer of the Mukdadiya Formation into the overlying sediments and its geochemical evolution is compatible with the type of saline minerals encountered in these sediments and the dominance of gypsum in them, which should be the first mineral to precipitate in this system. It should be noted here that brine exchange between the black mud slurry and the glauberite-rich mud facies is possible both ways.

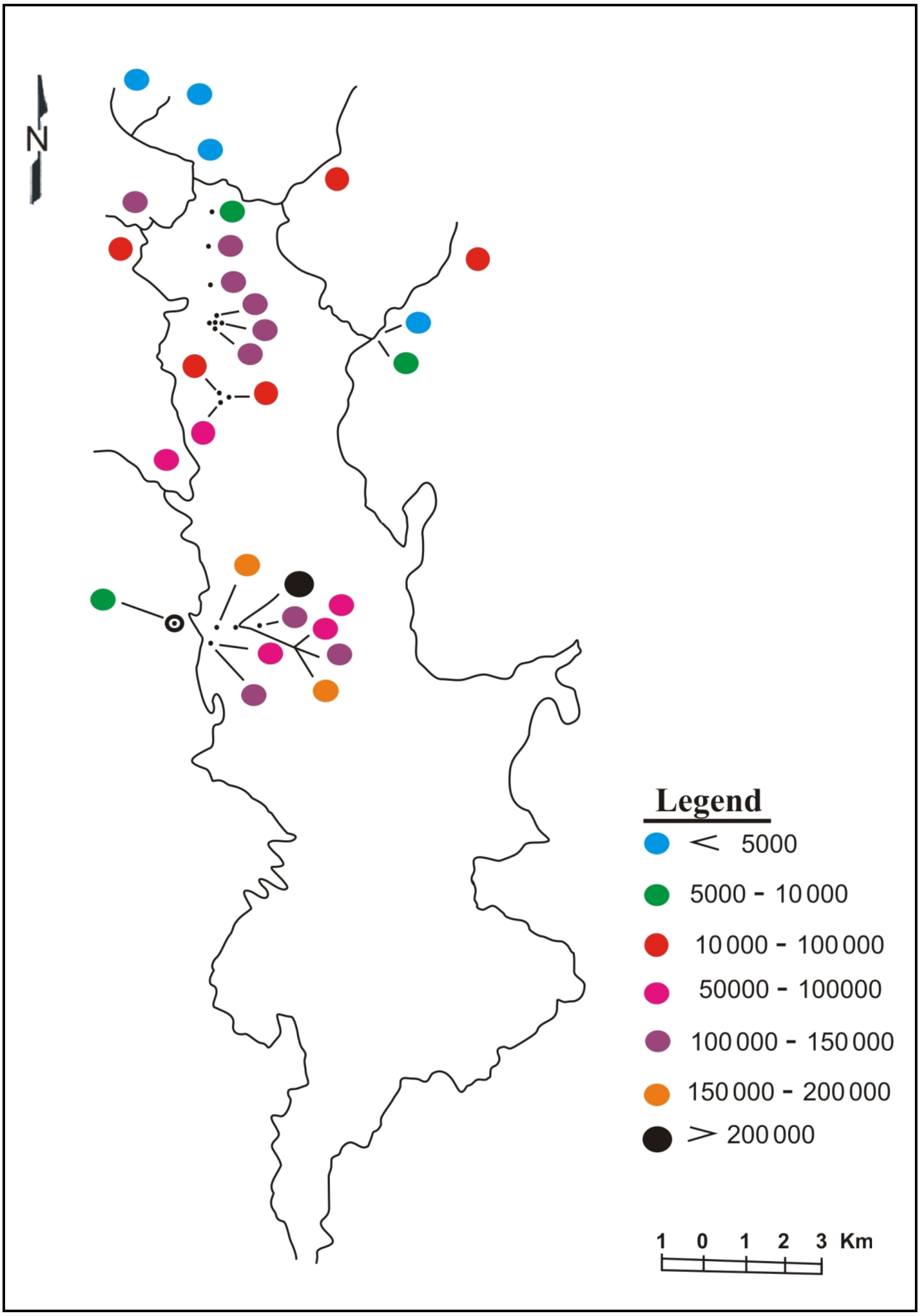


Fig.4: Dissolved solids concentrations in mg/l in water and brines from the Shari Playa basin

Table 1: Concentrations of the major components of the water and brines in the Shari Playa basin

		Perennial spring	Runoff water from Wadi Assam	Runoff water from Wadi Edmath	Ephemeral streams of the western side	Seepages brines	Brine from the Glauberite-rich mud	Water from Mukdadiya Fn aquifer	Playa Lake brine (early)	Playa Lake brine (late)	Saturated brine from the black mud slurry
Na^+	ppm	628	845	3427	2129	19155	38537	734	22663	65540	50414
	epm%	38.4	62.07	62.4	79.13	89.8	91.52	39.93	96.34	96.46	94
Ca^{2+}	ppm	521	3000	561	593	906	1002	523	589	641	869
	epm%	36.9	25.3	11.73	3.02	5.41	2.73	33.46	2.87	1.08	1.86
Mg^{2+}	ppm	2.4	88	744	2713	520	1228	244	69.3	775	1071
	epm%	23.8	12.25	25.64	17.64	4.58	5.52	25.71	0.56	2.16	3.78
K^+	ppm	9.0	8.0	21	94	107	165	4	91.8	349	317
	epm%	0.33	0.37	0.23	0.2	0.26	0.23	0.14	0.23	0.3	0.35
$SO_4^=$	ppm	2881	2281	8165	31019	11266	20	2275	28818	69643	3842
	epm%	85.3	80.16	71.19	53.56	22.18	22.87	60.37	58.66	49.08	3.58
Cl^-	ppm	248	345	2127	18735	29062	49484	2059	14889	53174	76217
	epm%	9.95	16.87	25.13	45.85	77.52	77.02	34.22	41.06	50.77	96.34
NO_3^-	ppm	–	–	80.06	–	–	–	–	–	–	–
	epm%	–	–	0.54	–	–	–	–	–	–	–
$CO_3^=$	ppm	18.0	9.0	12.0	142	10	37	9.0	24	54	18
	epm%	0.85	0.54	0.17	0.4	0.1	0.06	0.38	0.08	0.06	0.83
HCO_3^-	ppm	167	87	433	122	130	57	46	122	152	16
	epm%	3.9	2.34	2.97	0.18	0.24	0.05	1.01	0.2	0.08	0.04
pH		8.2	7.7	7.5	9.0	7.6	8.0	7.5	8.0	8.2	7.9
T.D.S.	Mg/l	5108	3960	17320	80426	65128	119270	5598	67250	197790	156080

Table 2: Possible evolution of brines (from water sources to resultant) in the Shari Playa basin, and the probable mineral phase whose precipitation could produce the changes

Water Source	**Probable resultant brine**	**Major change of brine composition relative to source**		**Precipitated mineral**
		Enrichment	**Depletion**	
Ephemeral water	Early and late playa lake brine	Na^+, K^+, Cl^-	Ca^{2+}, Mg^{2+} $SO_4^=$	Gypsum
Early playa lake brine	Late playa lake brine	Mg^{2+}, K^+, Cl^-	Ca^{2+}, $SO_4^=$	Gypsum
Late playa lake brine	Black mud slurry	Mg^{2+}, Cl^-	Na^+, $SO_4^=$	Glauberite and Thenardite
Black mud slurry brine	Brine from the glauberite-rich mud	Ca^{2+}, Mg^{2+} $SO_4^=$	Na^+, Cl^-	Halite
Ephemeral streams water	Brine from the glauberite-rich mud	Na^+, Cl^-	Ca^{2+}, Mg^{2+}, K^+, $SO_4^=$	Gypsum
Mukdadiya Fn aquifer water	Brine from the glauberite-rich mud	Na^+, Cl^-	Ca^{2+}, Mg^{2+}, $SO_4^=$	Gypsum
Brine from the glauberite-rich mud	Black mud slurry brine	Na^+, Cl^-	Ca^{2+}, Mg^{2+}, $SO_4^=$	Gypsum
Seepage brine	Early and late playa lake brine	Na^+, $SO_4^=$	Ca^{2+}, Mg^{2+}, Cl^-	Gypsum

Evolution of seepage brines into the playa lake brines shows an enrichment in Na^+ and $SO_4^=$ and a depletion in Ca^{2+}, Mg^{2+} and Cl^-. While Ca^{2+} and Mg^{2+} chlorides were not detected in the studied sediments, and therefore, this pattern could not be explained by their precipitation. Selective dissolution of thenardite and glauberite from the salt crust is possible but unlikely explanation, because of the presence of the highly soluble halite in the crust. Therefore, it seems that seepages contribution to the playa lake is too small to effect its composition or show an evolutionary relation with it. This is supported by the fact that the seepages are neither able by themselves to maintain the lakeafter the winter months nor keep the depression sediments wet in the drought years. Similarly, perennial springs on the northern periphery of the playa are with low yield to maintain a flow of water into the playa and thus are considered to be of no or little effects on the composition of the playa lake brine.

The correlation coefficients among different parameters are shown in Table (3). Many relations with significant values of correlation coefficient (over 0.7) for the number of samples used (Murdoch and Barnes, 1985) are revealed in this table. The pH of the playa lake brine shows significant positive correlation coefficient with $CO_3^=$. This is due to the fact that $CO_3^=$ concentration in the brine is considered to be a function of alkalinity. $CO_3^=$ ion may react with H ion below pH = 8.2 to form HCO_3^- (Butler, 1964, Davis and DeWiest, 1966 and Todd, 1970). This relation is reflected by the significant negative correlation coefficient between $CO_3^=$ and HCO_3^- (Table 3).

Table 3: Correlation coefficients between the analyzed constituents of the Shari Playa lake brine

	pH	T.D.S. mg/l	Na+ epm	K^+ epm	Ca^{2+} epm	Mg^{2+} epm	Cl^- epm	$SO_4^=$ epm	$CO_3^=$ epm	HCO_3^- epm	Ni ppm	Cu epm	Zn epm	Cd epm	Pb epm	Li epm	Br epm
Br	0.08	0.83	0.85	0.82	0.04	0.49	0.86	0.79	0.45	-0.11	0.39	0.02	-0.02	0.51	0.74	0.63	1.00
Li	-0.21	0.69	0.72	0.71	0.04	0.50	0.68	0.73	0.08	0.26	0.31	0.37	0.17	0.47	0.60	1.00	
Pb	0.19	0.79	0.74	0.81	0.39	0.54	0.69	0.78	0.51	-0.12	0.73	0.33	0.27	0.87	1.00		
Cd	0.28	0.62	0.61	0.61	0.41	0.49	0.57	0.65	0.54	-0.20	0.04	0.40	0.57	1.00			
Zn	0.17	0.87	0.12	0.08	0.09	0.47	0.07	0.18	0.14	0.005	0.18	0.27	1.00				
Cu	-0.47	-0.09	-0.05	-0.03	-0.26	-0.01	-0.04	-0.06	-0.20	0.16	0.41	1.00					
Ni	0.17	0.50	0.48	0.47	0.39	0.27	0.47	0.47	0.42	-0.15	1.00						
HCO_3^-	-0.65	-0.08	-0.06	-0.01	-0.41	0.30	-0.06	-0.04	-0.80	1.00							
$CO_3^=$	0.78	0.56	0.54	0.54	0.59	0.16	0.52	0.54	1.00								
$SO_4^=$	0.28	0.98	0.97	0.95	0.36	0.67	0.92	1.00									
Cl^-	0.18	0.94	0.98	0.90	0.15	0.57	1.00										
Mg^{2+}	0.19	0.64	0.63	0.60	0.005	1.00											
Ca^{2+}	0.60	0.34	0.24	0.37	1.00												
K^+	0.244	0.96	0.94	1.00													
Na^+	0.23	0.98	1.00														
T.D.S	0.27	1.00															
pH	1.00																

No. of Samples = 17
Significant Value = 0.55

Chloride and sulphate also show strong positive correlation coefficients between them and with Na^+ and K^+ due to their tendency to be precipitated at the late stage of precipitation as T.D.S. increases.

Calcium and magnesium ions, in the playa lake did not show significant correlations with all the parameters. This is probably due to the precipitation of their salts (carbonate and sulphate) in the early stage of ponding.

Davis and DeWiest (1966) stated that all elements are soluble in water to at least a small degree, even though natural concentrations are small that they may be difficult to be measured. In this sense, the trace elements, Ni, Cu, Zn, Cd, Pb, Li, Ba and Br have been analyzed and studied in this work on the lake brine.

Concentrations of Cu, Zn and Cd were below 1 ppm and therefore, were excluded from discussion.

Analysis of B and I were not obtained due to technical difficulties. The remaining bromine left after magnesium bromide precipitation shows significant to strongly significant positive correlation coefficients with Na^+, K^+, Cl^- and $SO_4^=$ in the brines, because of their similar tendency to be precipitated at the late stage of precipitation

due to the high saturation point of their salts. Bromide salts are usually highly soluble in water; therefore, precipitated bromide salts that found in the Shari Playa sediments (Black mud slurry), are dissolved in playa lake brine of the next winter; resulting in recycling and concentration of Br in the playa lake brine and the sediment's pore brine of the glauberite mudflat.

Lead (Pb) shows significant positive correlation coefficients with Na^+, K^+, Cl^-, $SO_4^=$ and Br. Due to the similarity in the ionic radius of Pb and K^+, they show similar behavior in brines and may substitute for K^+ in its minerals (Rankama and Sahama, 1950). Therefore, Pb shows significant positive correlation coefficients with the ions that usually persist in solution to the late stage of precipitation, such as Na^+, CI^-, $SO_4^=$ and Br.

Nickel (Ni) shows significant positive correlation coefficients with Pb and Cd. These correlations are due to that all these elements are a chalcophile elements and therefore have similar behavior (Rankama and Sahama, 1950).

Li shows positive correlations with Na^+, K^+ and CI^- due to incorporate their salts some Li (Rankama and Sahama, 1950). It tends, together with halite and thenardite of the salt crust to dissolve in the dilute water of the next winter and is precipitated again in the late stage of precipitation.

Bromine is recycled and concentrated in the playa lake and black mud slurry brines due to the high solubility of its salts, which led to the formation of magnesium bromide [$Mg_2(OH)3Br.4H_2O$] in the black mud slurry. This study has proved for the first time the natural presence of this mineral, which reported to be a synthetic mineral.

Factor analysis is appliedto investigate the interrelations in a matrix of correlations between variables (R-mode). Therefore, the playa lake brine parameters were processed by R-mode factor analysis in an attempt to find out the processes or sources may affect this brine. The playa lake brines were chosen from other brines in the Shari Playa basin to be analyzed by this method. Other water and brines collected from the area were not analyzed because they were represented by a relatively small number of samples.

This study revealed two effective factors, which account for 84.4% of the total variance (Table 4). The first factor (Fl) affects 59.36% of the total variance and represent the positive effect of T.D.S., N^+, K^+, CI^- and $SO_4^=$,due to their increase in concentration because of evaporation of the brine, and referring to soluble salts that have high solubility in water. The second factor (F2) affects 25.05% of the total variance (Tabel 4) and may represent the positive effect of the pH, Ca^{2+} and $CO_3^=$. This factor reveals that $CaCO_3$ is formed after the pH increases, which come on the expense of HCO_3^-, which is shown by its negative presentation, while pH, Ca^{2+} and $CO_3^=$ are positive. This factor reveals the increasein concentration of Ca^{2+} and $CO_3^=$ due to the dissolution of carbonates of Fatha, Injana and Mukdadiya formations, which are exposed at Himreen Mountain in the northeastern part of the catchment area. The third factor (F3) listed in Table (4) has small effect on the total variance. It affects 7.0% and represents HCO_3^- only, which is most probably supplied by rain water. Therefore, this factor represents meteoric water effect. Plotting the three factors against each other (Fig.5) shows the soluble salts group (Fl), the calcium carbonate group (F2) and bicarbonate group (F3). From plotting F1 against F2, the

components of one group are located close to each other in one cluster, which indicates the possibility of these ions to form salts of different compounds depending on the saturation index of the ions.

The presence of calcium carbonate group revealed that it has been participated in the formation of the carbonate minerals upon the increase in brine concentration by evaporation. These ions (Ca^{2+} and $CO_3^{=}$) may also reveal their original supply to the playa lake, probably by Assam ephemeral stream, which shows higher content of these ions than the other water and brines supplied to the playa basin. On the other hand, when plotting Fl against F3 (Fig.5), the components show a cluster around Fl composed of the most soluble ions, whereas HCO_3^{-} shows its location away from the other variables and close to F3. This kind of distribution indicates that the variables of Fl are the most effective constituents in the brine of the playa lake. HCO_3^{-} indicates the effect of meteoric water on the playa lake brines as shown in F3.

Table 4: The rotated factor matrix of (R-mode) factor analysis
for the Shari Lake brine

	Fl	**F2**	**F3**
pH	0.11	0.92	– 0.04
T.D.S.	0.96	0.20	0.09
Na^{+}	0.98	0.12	0.04
K^{+}	0.94	0.20	0.07
Ca^{2+}	0.13	0.82	0.05
Mg^{2+}	0.61	0.10	0.66
Cl^{-}	0.98	0.05	– 0.03
$SO_4^{=}$	0.94	0.22	0.16
$CO_3^{=}$	0.47	0.75	– 0.39
HCO_3^{-}	– 0.02	– 0.65	0.71
Eigen value	5.93	0.50	0.70
Percent of trace	59.36	25.05	7.0

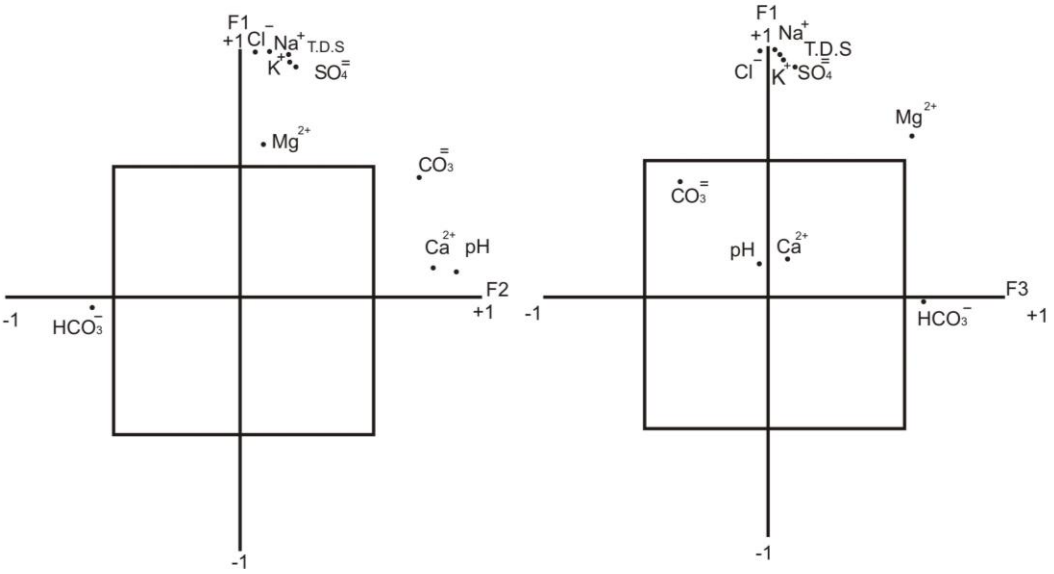


Fig.5: The relation between the factors of the R-mode factor analysis
for the brine of the Shari Playa Lake

The factor analysis shows in its two effective factors that Na^{+} – Cl^{-} – $SO_4^{=}$ facies are the most predominant water type in the playa lake brine, while Ca^{2+} – $CO_3^{=}$ facies type acts as a subgroup among the major facies determined by Fl. The occurrence of such facies and its sources were found to be identical with the results obtained from the trilinear diagram (Fig.2) and the method of Korlov (Matthess, 1982), which has been used for water classification.

R-mode cluster analysis dendogram is constructed for the brineof the Shari Playa Lake (Fig.6). Similar to the R-mode factor analysis, it revealed three effective clusters. They are in order of their similarities in strength: T.D.S., $SO_4^{=}$, K^{+}, Na^{+} and CI^{-} cluster, pH, $CO_3^{=}$ and Ca^{2+} cluster and HCO_3^{-} cluster. The first cluster indicates cations and anions that may form salts upon evaporation of the brine and represents the component of the salts that have high solubility. The second cluster indicates the increase in the calcium and carbonate ions concentrations probably by the effect of the water brought into the Shari playa by Wadi Assam, which shows relatively higher concentrations of Ca^{2+} and $CO_3^{=}$ than other water sources. Ca^{2+} and $CO_3^{=}$ increase may ultimately be accompanied by an increase in the pH values, i.e. alkalinity increase of the brine. The third cluster indicates the effect of HCO_3^{-}, which is supplied by rain water. The presence of this cluster in the highest level of similarity indicates its small effect among other clusters. It has been found that the results from this analysis coincide with those of the factor analysis of the same brine.

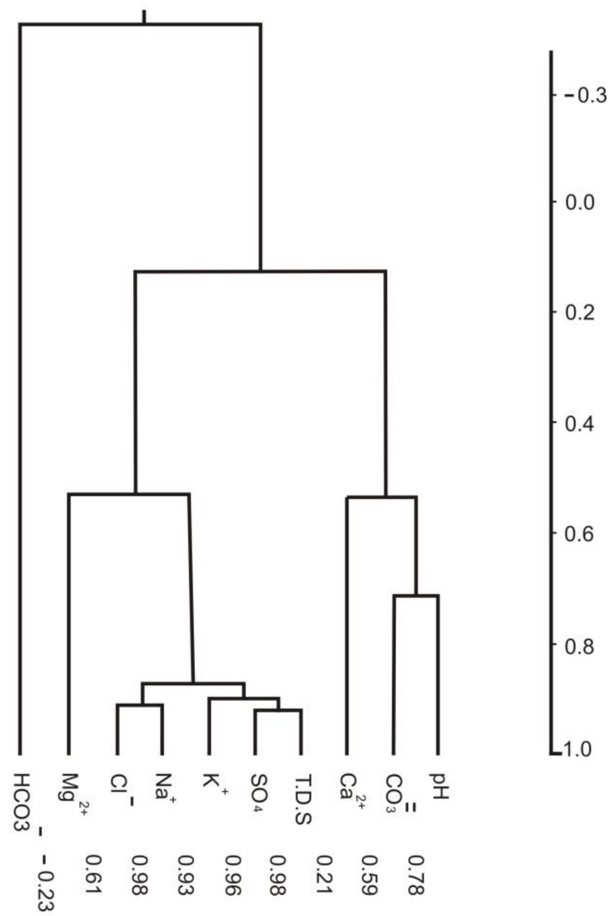


Fig.6: Dendogram of R-mode cluster analysis for the brine of the Shari Playa lake

CONCLUSIONS

- Recent observation of the Shari Playa Lake proved that the rain water falling on the catchment area is the most effective water resource.
- Most water and brines from the Shari Playa basin are characterized, by the dominance of the alkalis $Na^+ + K^+$ and the $Cl^- + SO_4^=$. Other water types also occur but of minor importance.
- Comparison of water and brine compositions shows that they are generally genetically related. Ephemeral stream water has evolved to the lake brine by gypsum precipitation. The same path is true for the evolution of the ephemeral stream water into the glauberite-rich mud pore brine. Similarly, the lake brine may evolve into the black mud slurry brine through the precipitation of glauberite and thenardite. This brine may (in turn) evolve into the glauberite-rich mud pore brine through the precipitation of halite. The other less important source is the Mukdadiya Formation's aquifer water, which may evolve into the overlying brine of the glauberite-rich mud through the precipitation of gypsum in the underlying sediments, which is rich in gypsum.
- Trace elements are of very low concentrations in the lake brine due to their low solubility, except for Br where it is recycled and concentrated in the playa lake and black mud slurry brines due to the high solubility of its salts, which led to the formation of magnesium bromide [$Mg_2(OH)_3.4H_2O$], which has not detected naturally before.

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