HYDROGEOCHEMISTRY AND BRINE EVOLUTION OF MAHARLOU SALINE LAKE, SOUTHWEST OF IRAN

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ABSTRACT: Maharlou Lake, located in southwest Iran, is an intra-continental sedimentary basin. Its area is about 280 km² with an average water depth of 1.5m during wet seasons. The water level in the lake is controlled by several factors, including runoff from Maharlou catchments, groundwater seepage, and direct rainfall over the lake and the evaporation rate. Hydrochemistry of the catchments water resources showed mainly chloride and sulfate waters due to the geology of the surrounding areas and its variable lithology. Hydrochemical investigations were carried out over a time period from 1975 to 2002 using previously published analysis, together with newly collected water samples. Two hundred thirty samples were collected during summer 2002 and spring 2005. Results showed distinct changes in the brine type over time; from $Mg-SO_4-Cl$ type reported in 1970 to a recent $Na-Mg-Cl-(SO_4)$ type, which is comparable with Great Salt Lake in the USA. A Change in diluted water composition going from $HCO_3 \geq Ca + Mg$ to $HCO_3 \ll Ca + Mg$ has taken place. That is, the path of brine composition on the Eugster and Hardie flow diagram has changed from row III_{2b} to the path II, and may finally result in a $Ca-Na-Cl$ or $Na-SO_4-Cl$ brine type in the future. In this study, two mixed zones of fresh and saline waters were recognized in the northwest and center of the lake, with the lowest ionic concentrations, located where there is significant river and ground water supply.

Keywords: Hydrogeochemistry, brine, Maharlou, Saline Lake, Iran

INTRODUCTION

Maharlou Lake is an ephemeral saline lake and according to the Sonnenfeld classification scheme (1991), and is regarded as an intra-continental basin. Krinsley (1970) divided the Shiraz (Maharlou) playa into 3 parts including an intermittent lake, salt pan and mud flat involving a narrow beach zone. He also chemically analyzed the major constitute elements of the lake. According to his studies, Maharlou Lake includes 54% of the whole body of Shiraz playa and comprises a quite shallow intermittent lake in the center of the Shiraz basin. Except the invaluable hydrochemical data reported by Krinsley (1970) no detailed investigation on the hydrochemistry and brine evolution of the lake was carried out before this study. A dry period between the years 2001 and 2002 and an ensuring wet period in 2005 resulted in an extraordinary evolution of the water which was revealed this study.

REGIONAL SETTING

Maharlou Lake is located southeast of Shiraz, Iran (Fig. 1). In wet seasons, the Lake in its largest size is 26 km long and 12 km wide covering an area of 280km². The Maharlou basin is situated in a relatively elevated depression (1455 m above sea level) with a northwest-southeast trend. Maharlou Lake forms in t he lowest part of the basin. A relatively small number of ions, all of them derived from the weathering of the outcrops on the lake catchments, comprise the bulk of the dissolved solids content of unsaturated river waters that enter the lake. There is no permanent river running into the lake but the drainage system is composed of ephemeral rivers including Nahre-Azam (or the Khoshk River) and Chenare-Rahdar (or the Babahaji) streams. The latest, with the largest discharge plays the most important role in the hydrochemical composition of the Maharlou Lake.

There are 10 major springs in the Maharlou basin as well as some other smaller springs in the western side of the lake (Fig. 1). Groundwater from the Shiraz aquifer, located in the north side drains directly into the lake. The average annual minimum, maximum temperature, and precipitation of the area are respectively 9.8°C, 25.6°C and 341mm, with the maximum precipitation occurring in January and December. The average annual evaporation rate is about 2391 mm. The average depth of water in the northern part of the lake at time of sampling in the wet period was about 1.9 meters.

The Maharlou basin is located in the folded Zagros zone including closed anticlines with a NW-SE trend. Outcrops in the lake catchments, mainly involves sedimentary rocks including the Precambrian Hormoz salt and Gypsum diapiric outcrops as the oldest successions in the study area, Bangestan Group, Gourpi, Tarbour, Pabdeh, Sachun, Jahrom, Asmari, Mishan, Razak, Aghajari and Bakhtiyari Formations composed of limestones, shales, dolomites and sandstones (Fig. 2). Water resources organization of Fars (1995) ran geoelectric survey to determine thickness of alluvium, sedimentary layers and fractured zones and recognition of faults and tectonic axises as well as defining dynamic modules of the Allaodoleh Dam located to the northern coast of the Maharlou saline lake. According to this study, Razak formation forms the lake floor which includes limestones. Deep drillings by the Earth sciences developing company (23m) shows unlithified sediments to this depth. However core recovery was low and the obtained cores were of a very poor quality which could only provide general sedimentological information of the middle part of the lake. Results are indicative of occurrence of mud laminae including gypsum and halite crystals to a depth of 7 meters, a thick salt layer with a very low mud content from depth of 7 to 13 meters and again mud layers with Gypsum
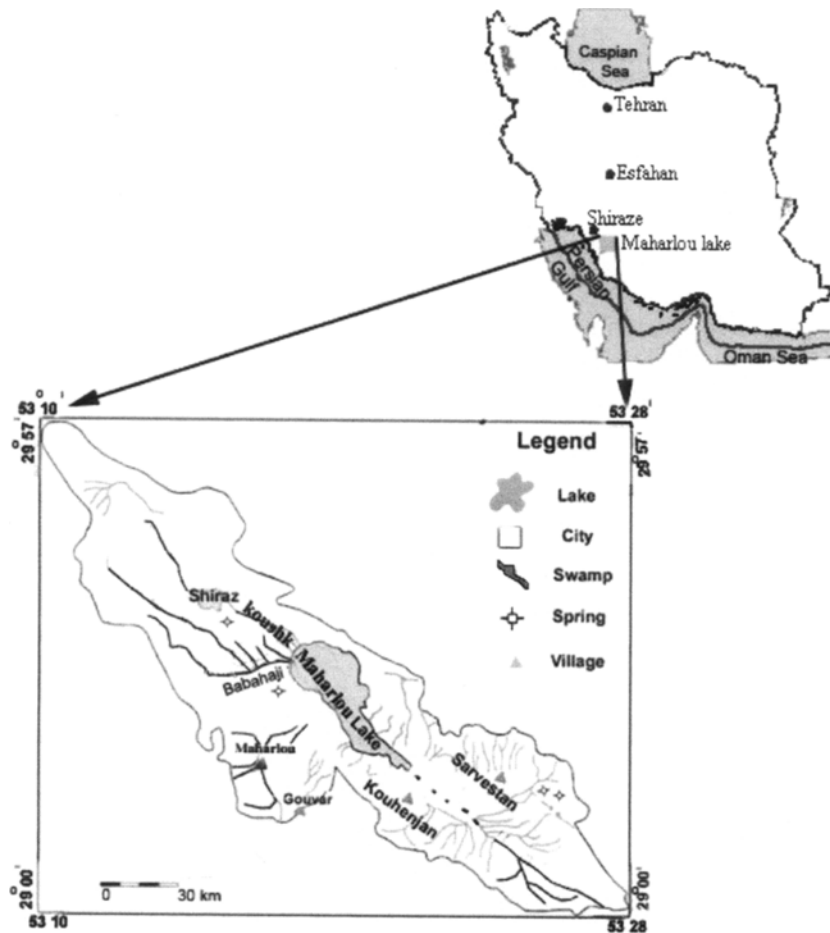
Figure 1. Hydrographic map of the Maharlou Basin. Nahr-e-Azam (Khoshk) and Chenar Rahdar Rivers are more important than others.

and Halite crystals from depth of 13 m downward (Shariati Bidar 2001). Chemical analysis carried out on the sediments derived from each 1 m of the obtained cores by measuring the amount of Na^+, K^+, Ca^{++}, and Mg^{++} cations and Cl^- anion. Therefore, unfortunately results of the chemical analysis are not very informative. According to the seismotectonic map of Iran (Berberian 1983) the Sarvestan left-lateral fault passes through the lake with a NW-SE trend. The fault has been active during Quaternary and played an important role in the formation of the lake (Shahrabi 1994); therefore it can be considered as a tectonically related lake.

MATERIALS AND METHODS

As the first step, the required dataset was prepared using all existent data including topographic and geological maps, as well as different hydrological, hydrogeological and sedimentological data.

Sampling was carried out using a 2x2 km grid according to the well established Hakanson and Jansson formula (1983) for lake sampling. Water samples from each cell of the established were collected in both dry and wet seasons in

vertical profiles: one from surface water and the other from sediment and water interface. The brine samples were collected in 200 ml bottles that had been pre washed in double distilled water before sampling. They were stored at a constant temperature of 0°C (following the techniques established by Bryant et al. 1990). Water samples were also collected from drainage systems that run into the lake, springs, wells, as well as groundwater sources. Each sample was divided into 2 separate samples before being sent to the laboratory to enhance the accuracy of the results. At the time of sampling, lake depth, the physical and chemical parameters of the water samples including the amount of dissolved oxygen (DO), conductivity (EC), total dissolved solids (TDS), pH and salinity were measured using a Hach Sension system model 156 multi-parameter Meter, following a standard operating procedure explained by California State Water Resources Control Board (2002). Several autours reported results using the device (e.g Suangkiattikum 2005; Ermilio 2005; Ikhu-Omoregbel et al. 2005; Hunt et al. 2006). The accuracy of the multi probe device was also checked by the Geological survey of Iran Hydrochemistry team in Chabahar bay and Oman Sea, comparing the obtained results with the availabe CTD
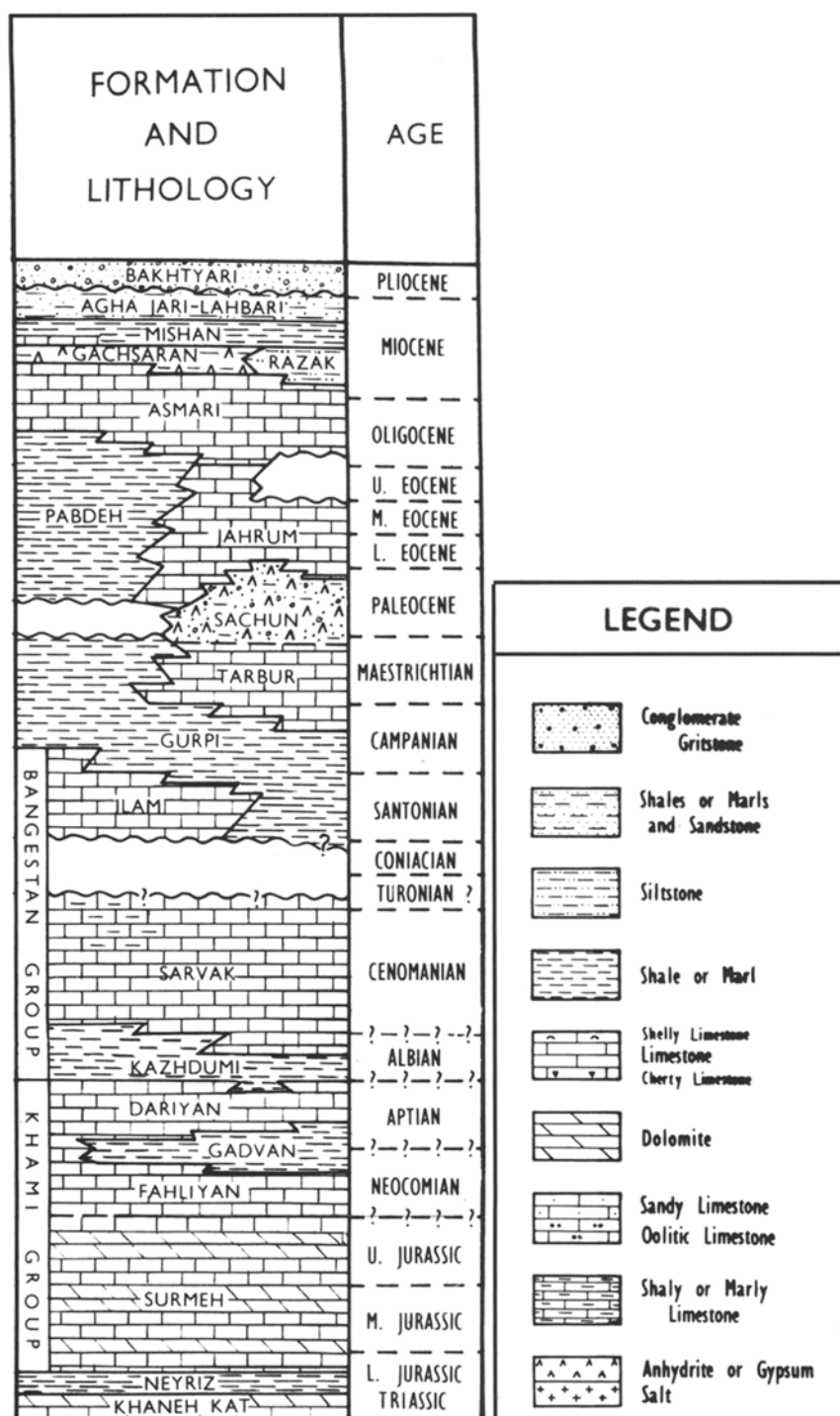
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Figure 2. Stratigraphic units of Fars province of Iran (slightly modified after James and Wynd 1965).

data provided by Idronaut for 50 samples (Sharmad 2005). In addition, due to the problem caused by high salinity to the standard pH electrodes which are designed for use in low-ionic-strength solutions (Lewis and McConchie 1994) pH indicator papers were used to controle the obtained pH values. Major components were analyzed on an automated Knauer Ion chromatograph with Hamilton x100 for anion and Hamilton x200 for cation columns in the Geological Survey of Iran, similarly utilized by several authors (e.g

Borgarello et al. 1986). The mineralogy of the salt crut was determined by runnig whole samples on a Philips X-ray diffractometer using standard methods (e.g Bryant et al. 1994)

RESULTS AND DISCUSSIONS

To determine the type of brine, after measuring cations and anions concentrations, these amounts were plots on the

Piper Diagram

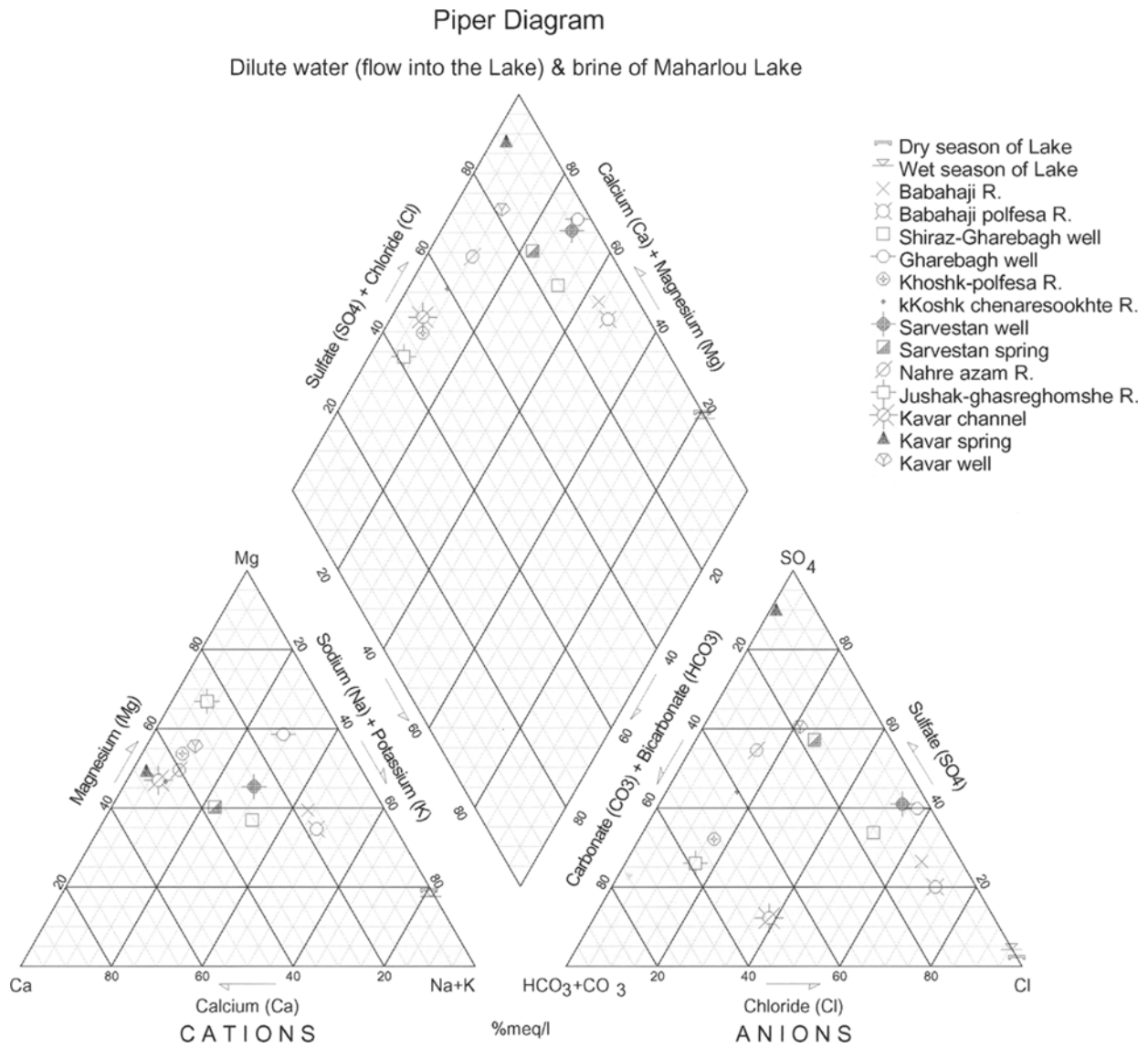### Dilute water (flow into the Lake) & brine of Maharlou Lake

Figure 3. Piper diagram of major elements of dilute water and brine. Brine compositions during wet and dry seasons are all plotted near one of the corners of the piper diagram, anions close to the Cl corner and cations close to the Na+K corner.
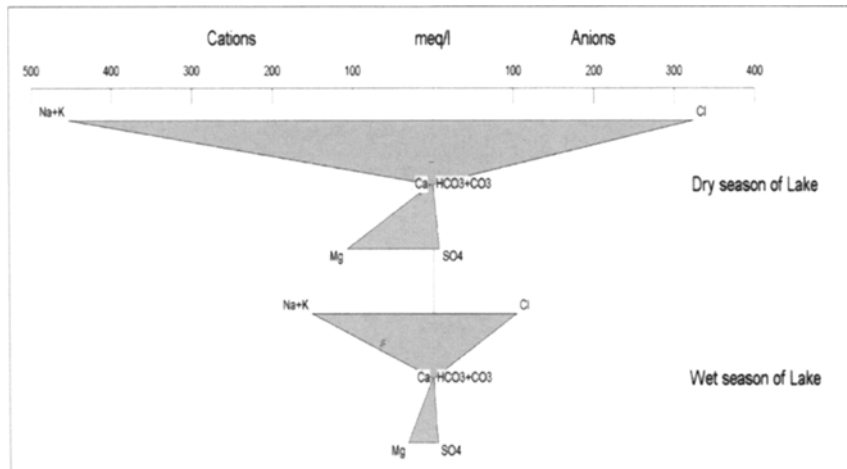

Figure 4. Average of major elements of the Maharlou brine is plotted on the Stiff diagram. It shows that chloride is the most important anion and sodium is the most important cation of the brine during wet and dry seasons.

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ternary diagram developed by Piper (1994) and the Stiff diagram (Fig. 3 and 4). The plots can be used to display the relative abundances of major anions and cations in dilute natural inflow waters and the concentrated brine of their associated closed-basin lakes (Hardie and Eugster 1970).

According to these plots the brine is currently a Na-Mg-Cl-(SO_4) type.

Maps of distribution some cations and anions water lake (Fig. 5) shows a decrease in percentage of the ions in two
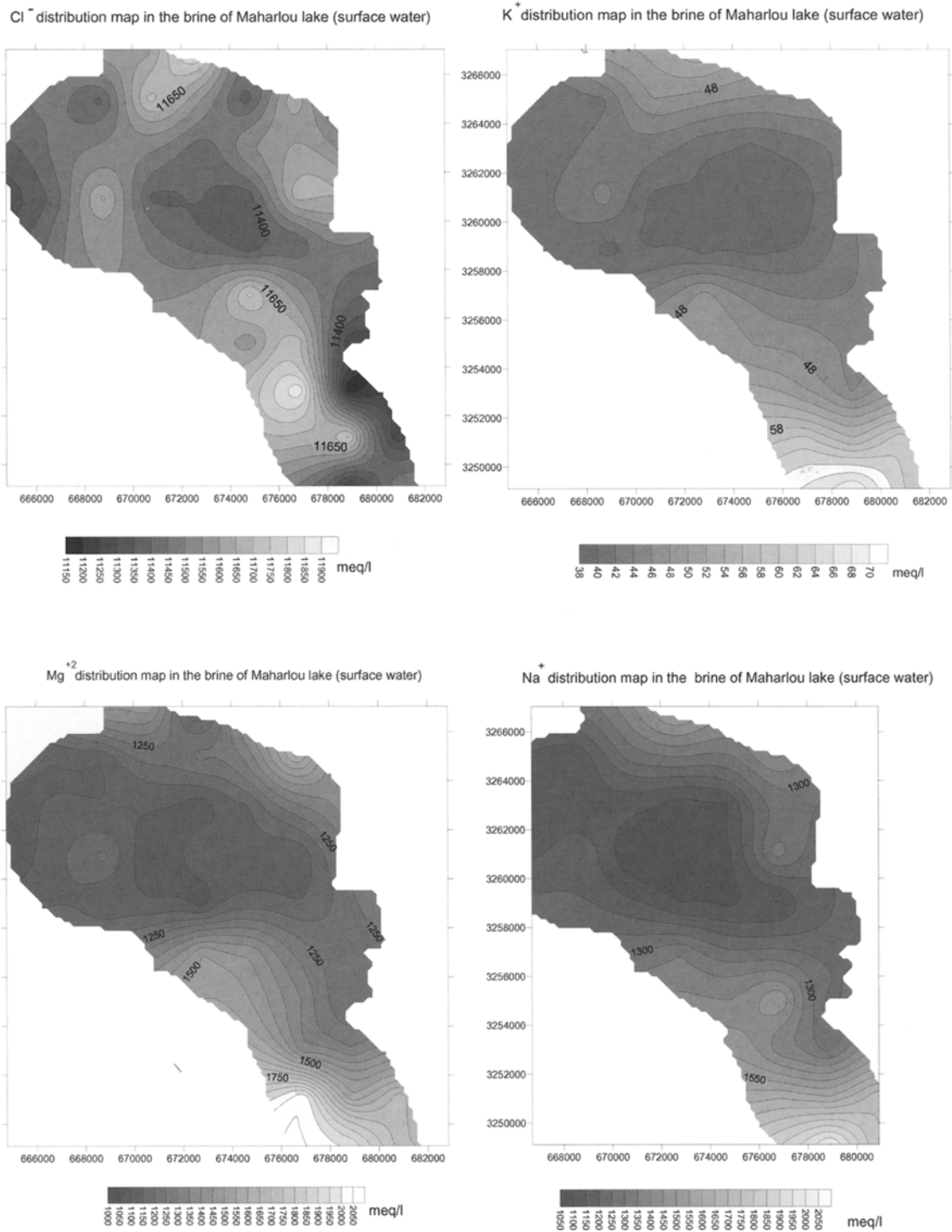

Figure 5. Distribution maps of some cations and anions of the lake, showing a major decrease in percentage of ions in two parts (northwest and western margin) of the lake.

parts of the lake where fresh water from the Babahaji River in the northwest and springs on the margin of the lake, flow into it. Mixing of fresh and saline waters resulted in the dissolution of evaporates in these places. This is also obvious on the ETM satellite images of the lake (Fig. 6). The new types of waters flowing into the lake were also determined. Hydrochemical analyses of these waters showed that the difference of cations and anions is a cause for the different geological features (e.g Jones and Decoampo 2004). The amount of calcium and magnesium cations and sulfate and chloride anions are dominant. It should be noted that in all the input waters, the total amount of Ca and Mg exceeds the amount of HCO_3; $HCO_3 \ll Ca + Mg$. This means that evolution path II of the brine evolution flowchart (Eugster and Hardie 1978) eventually create a $Na-SO_4-Cl$ or $Ca-Na-Cl$ brine type, whereas the current brine is $Na-Mg-Cl-(SO_4)$ which belonged to the path III_{2b} of the mentioned flowchart. The current Maharlou Lake brine type is similar to Great Salt Lake in the USA (Spencer et al. 1985; Domagalski et al. 1989). Relative amounts of ions in dry and wet seasons are as follows: $Na > Mg > K > Ca$ and $Cl > SO_4 > HCO_3 > CO_3$ (Fig. 7). Due to high concentrations of sodium and chloride, on the surface of the lake, salt crusts are developed during the dry season. In the wet season, dissolution of salt crusts increases lake water concentration. In the summer, large amounts of evaporite minerals precipitate to the lake floor (Sonnenfeld 1984). The largest amount of salty crust precipitated in the summer of 2002, when it reached a thickness of 60 cm. During wet seasons, diluted waters entering the lake dissolve a major portion or even the whole salty crust. Mineralogy composition of the salty crust, in the dry condition is only Halite whereas in wet conditions a variety of evaporite and carbonate minerals are precipitated; among which Halite, Gypsum and Calcite are the most abundant.

Major changes in brine type during short periods are also of significance where the type of brine totally changed within approximately 32 years. Krinsley (1970) reported the concentration of the lake ion components as follows; $Cl^- = 5320$ ppm, $Na^+ = 5200$ ppm and $Mg^{++} = 339040$ ppm. These values were converted to meq/ lit, and a comparison with the current cations and anions constituents of the brine (Table 1), indicates the amount of Mg was much greater than its current level. This difference means that by 1970, saturation of the brine had increased and salinity had gone up to 350 g/lit. Consequently Halite precipitated. As a result the percentage of Na^+ and Cl^- content of the brine decreased and Mg^{++} and SO_4^- decreased (Warren 1999).

Physicochemical parameters including TDS, EC, DO and pH of the input waters and the brine, measured during the wet season is presented in Table 2. Recorded pHs are indicative of a weakly alkaline environment. Salinity changed from 135gr/lit during the wet status to 355gr/lit during the dry period.

CONCLUSION

The Maharlou saline lake brine type has changed very rapidly in recent decades. Results suggest a change in the type of brine from an $Mg-SO_4-Cl$ type in 1970 to a Na-Mg-
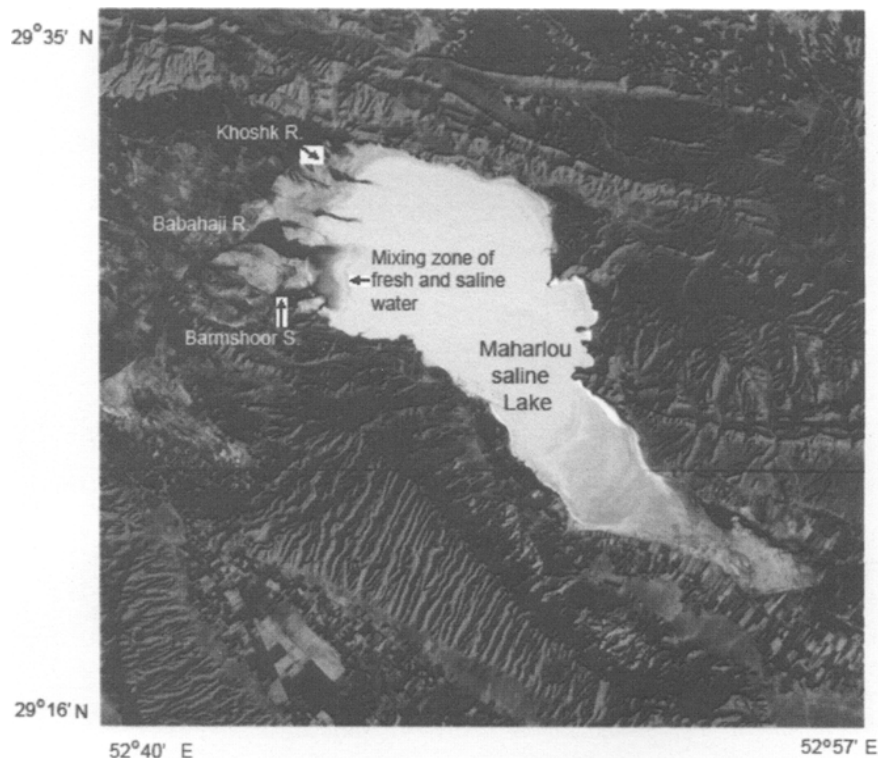

Figure 6. ETM Satellite images showing the mixing zone of fresh and saline waters
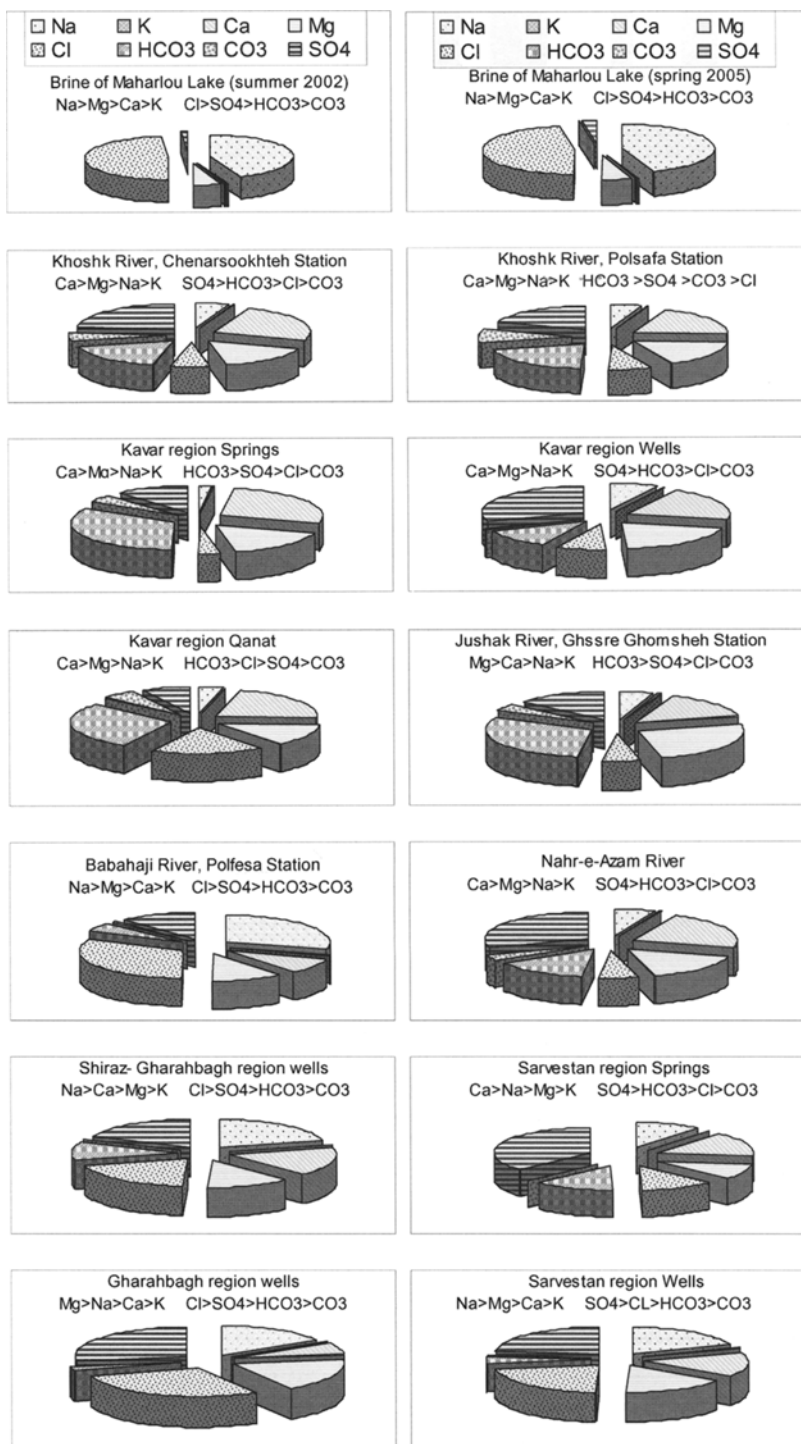
Figure 7. Cation and anion Pie Diagram show relative amounts of ions in dilute waters and the brine of Maharlou basin.

Table 1. Ions concentration measured in different years (in miliequivalents per liter) of brine.

Ions Year	Mg	Cl	Na
1970	56506	473	313
2002	1313	10409	11502
2005	396	3474	3671

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Table 2. Physicochemical parameters of the input waters and the brine, during the wet season.

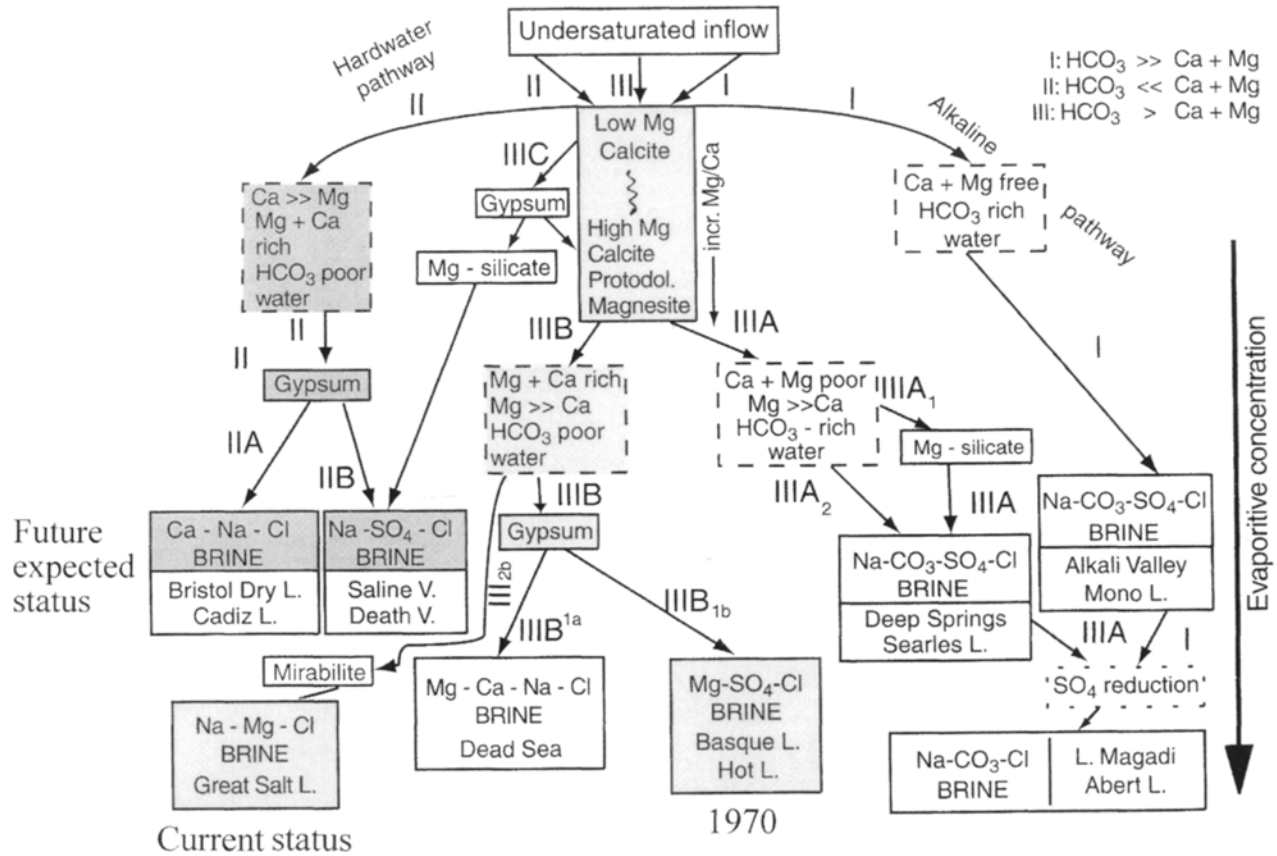|	Depth (m)	pH (Surface)	pH (Interface)	EC(mmuhs/s) (Interface)	EC (Interface)	TDS (ppm) (Surface)	TDS (ppm) (Interface)	DO (Surface)	DO(mg/L) (Interface)	T (°C) (Surface)	T (°C) (Interface)
Ave.	1.27	8.3	8.16	82.5	103.4	52.8	65.6	7.08	4.66	24.8	25.3
Max.	1.9	8.67	8.6	219.6	436.1	140	282	8.59	8.29	28.4	31.2
Min.	0.15	7.24	7.14	32.5	24.6	19.5	14.4	1.18	1.72	21.2	21.8

Figure 8. Flow diagram for the geochemical evolution of closed basin brines from Eugster and Hardie (1978). The brine type changed from Mg-SO$_4$-Cl type reported in 1970 to a recent Na-Mg-Cl-(SO$_4$) type (highlighted in light gray). A Change in diluted water composition going from HCO$_3$ ≥ Ca + Mg to HCO$_3$ << Ca + Mg has taken place which suggests a change in the path of brine composition from row III$_{2b}$ to the path II (highlighted in dark gray).

Table 3. Correlation coefficient between cations and anions in the Maharlou brine (Wet season).

	HCO$_3$	Cl	SO$_4$	Ca	Mg	Na	K	TDS
HCO$_3$	1	.166	.268	.109	.507	.149	-.077	.175
Cl	.166	1	.462	.590	.681	.991	.901	.993
SO$_4$	.268	.462	1	.259	.548	.493	.387	.497
Ca	.109	.590	.259	1	.401	.581	.592	.567
Mg	.507	.681	.548	.401	1	.629	.386	.683
Na	.149	.991	.493	.581	.629	1	.924	.989
K	-.077	.901	.387	.592	.386	.924	1	.909
TDS	.175	.993	.497	.567	.683	.989	.909	1

Cl-(SO$_4$) type at the present time. Then in the input waters HCO$_3$ exceeded the total amount of Ca and Mg (HCO$_3$ > Ca + Mg) while currently, all waters flowing into the basin are chemically HCO$_3$ << Ca + Mg despite the difference in percentage of their ion contents. Therefore the evolution path of the brine from input waters has changed from III$_{2b}$ of the flow diagram for the geochemical evolution of closed basin to the path II (Fig. 8). That is, the brine type is expected to change to Na-SO$_4$-Cl or Ca-Na-Cl in the future (Fig. 8). A glance at figures 3 and 4 reveals that the brine compositions during the wet and dry seasons all plotted near one of the corners of the piper diagram, anions are close to the Cl corner, and cations are close to the Na+K corner.

The present water type of the Maharlou lake brine is more influenced .by the chemical composition of past input waters, probably because ions form as evaporites on the basin floor and are dissolved during the wet seasons. Statistical analysis, correlation coefficient, and cluster analysis of two distinctive periods show that the correlation between the constituent elements is very high during wet periods (Table 3) whereas in dry period the correlation is low due to geochemical diffraction of elements during evaporation as a result of formation and precipitation of evaporite minerals. Percentage of anions and cations in the northwest and center parts of the lake is highly decreased, due to fresh waters flowing into the lake, mixing of saline and fresh waters and the dissolution of the salty crust during the wet seasons.

ACKNOWLEDGEMENTS

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