Characterizing major controls on spatial and seasonal variations in chemical composition of surface and pore brine of Maharlu Lake, southern Iran

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Abstract

Maharlu Lake with Na-Cl water type is the terminal point of a closed basin in southern Iran. A total of 10 water samples from two rivers discharging to the lake and 78 water samples of surface and pore brine of Maharlu Lake have been collected from different depths (surface, 20, 50 and 100 cm) of four sampling stations along the lake during a period of lake water level fluctuation (November-2014 to July-2015). To investigate chemical interaction between lake surface-water and shallow pore-water, and to understand the major factors governing chemical composition of Maharlu brine, concentrations of major and minor (boron, bromide and lithium) solutes, pH and total dissolved solids (TDS) have been measured in collected water samples. Saturation indices of evaporite minerals in collected water samples have been also calculated. The chemical behavior of dissolved solutes and evaporative evolution of the lake brine during a hydrological period have been simulated using PHREEQC. The results of our investigations indicated that chemical composition of lake surface water and pore brine of Maharlu Lake are mainly connected with Lake water level fluctuations and distance from input rivers (and depth), respectively. Hydrochemical investigations and statistical analysis showed that the

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brines chemistry of Maharlu is mainly controlled by three processes: brine evaporative evolution, dissolution-precipitation and diagenetic evolution of secondary carbonates.

Keywords: Maharlu Lake, lake surface water, pore water, chemical composition

1. Introduction

The study of salt lakes is important in terms of paleoclimatology, investigation of ancient sedimentation environments, tectonic settings, extraction of economic evaporite minerals and concentrated minor elements, and their geochemical impacts on adjacent water resources and ecology (Torgersen et al. 1986; Smoot and Lowenstein 1991; Yechieli and Wood 2002; Lerman 2009). The most important prerequisite for the occurrence of salt lakes is that the rate of evaporation exceeds precipitation which is a characteristic of arid and semi-arid regions (Eugster and Hardie 1978). Topographical closed basins where evaporation is the only or predominant output of water are favorite places for occurrence of salt lakes (Deocampo and Jones 2013).

The chemical composition of a salt lake water is dominantly controlled by the interaction of original surface water with pore water, groundwater and sediments of the lake, and by evaporative concentration and chemical precipitation of relatively less-soluble evaporite minerals (Hardie and Eugster 1970; Eugster and Jones 1979; Torgersen et al. 1986). The chemical composition of chloride lakes go through significant alterations due to evaporation and a sequence of mineral precipitation (Kolpakova and Gaskova 2017). Additionally, diagenetic processes such as dolomitization of carbonates by Mg enriched waters (Warren 2000) and sulfate reduction can affect the chemistry of salt lakes (Torgersen et al. 1986).

The Maharlu Lake with an average elevation of 1425 meters above sea level (m.a.s.l) and a maximum area of 230 km^2 is located in the center of the Maharlu closed Basin, and it receives all surface water and part of the groundwater of the basin. The average salinity of Maharlu Lake water is 330 g/l. A significant amount of halite is extracted significantly from the lake for industrial and household uses. Subsurface intrusion of Maharlu brine to the adjacent aquifers has been reported by Tajabadi et al. (2017). This causes increasing salinity of groundwater in the surrounding aquifers.

According to hydrochemical and isotopic studies, Maharlu Lake brines originate from the extreme evaporation of former waters and loss of the relatively less-soluble salts (Zak and Gat 1975), which results in the formation of a thick salt crust on the lake floor. The fresh water enters the lake in the wet seasons through ephemeral rivers, direct runoff and direct precipitation on the lake surface. Lake surface water is formed from freshwater interactions with different parts of the lake such as mud flat, efflorescent crust and salt crust.

The major aim of this study is to investigate evaporative evolution of the Maharlu lake water and to evaluate the most important factors controlling lake water chemistry. Furthermore, the chemical composition of Maharlu Lake surface water (SW) and shallow pore water (PW) are investigated as a function of depth, distance from input rivers and lake water level (LWL) fluctuations.

2. Study area

2.1. Geological settings

The intracontinental (topographic) closed basin of Maharlu has an area of 4272 km^2 and is located in the simply folded zone of Zagros Orogeny in Southern Iran. The basin is an extended NW-SE geosynclinal structure surrounded by several high level carbonate anticlines mainly composed of Asmari-Jahrom Formation with age of Oligomiocene (Fig. 1).

The Maharlu Lake has a maximum area of 230 km^2 and an average elevation of 1425 meters above sea level (m.a.s.l). It is a playa lake formed in the lowest part of the basin. The age of the lake has been estimated to be 10 to 20 thousand years using the salt storage of the lake and geomorphological studies (Krinsley 1974; Shahrabi 1994).

The salt diapirs of Sarvestan, Fasa and Fedashkouh emerge in the east of the Basin due to the uplift of Precambrian salt rocks of the Hormuz Formation (Zarei et al. 2014; Mehdizadeh et al. 2015). These salt diapirs are the most likely sources of salinization in the eastern area of the basin (Zarei 2016; Nekouei et al. 2016; Nekouei and Zarei 2017). In addition, dissolution of the evaporite formation of Sachun (Paleocene-Eocene), mainly composed of gypsum, marl and limestone, is the main reason for

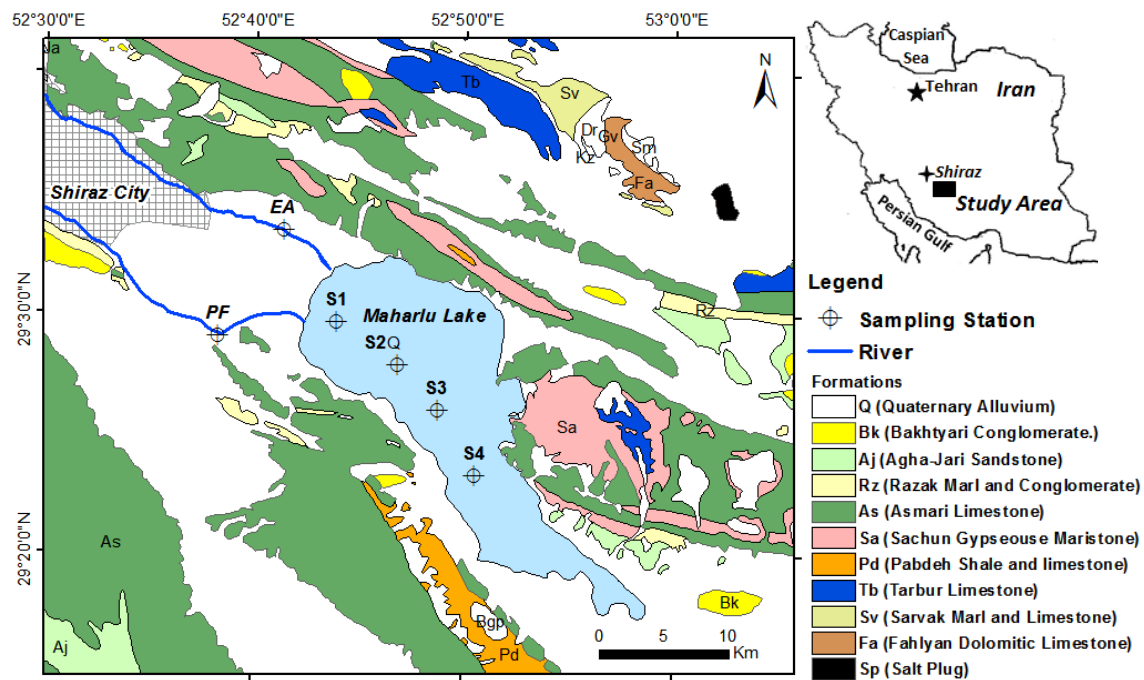formation of sulfate type waters in western parts of the basin (Zarei 2010; Kouchekzadeh and Zarei 2017).

Fig. 1 Geological map of the study area modified from the 1:250000 Shiraz Map (National Iranian Oil Company, second edition, 1979). PF and EA are the selected sampling stations on Babahaji and Khoshk rivers, respectively. Location of sampling stations along longitudinal axes of the lake to collect SW and PW are station 1 (S1), station 2 (S2), station 3 (S3) and station 4 (S4)

Shariati-Bidar (2001) reported a sequence of unconsolidated sediments in a 23-m deep core drilled in the central part of Maharlu Lake as: mud lamina associated with halite and gypsum minerals (0-7 m); thick salt layer with a slight mud content (7-13 m); and again mud lamina with gypsum and halite minerals to the end of the core. The mineralogy of the lake sediments is dominated by halite, gypsum, anhydrite, calcite, aragonite, dolomite, glauberite and aluminosilicate (Khosravi, 2018). However, geophysical investigations by the Fars Water Resource Organization (1995) indicate that the unconsolidated sediments of the bottom of the Maharlu Lake are underlain by bedrock from the Razak Formation. The Razak formation is mainly composed of marl and shale from the Miocene.
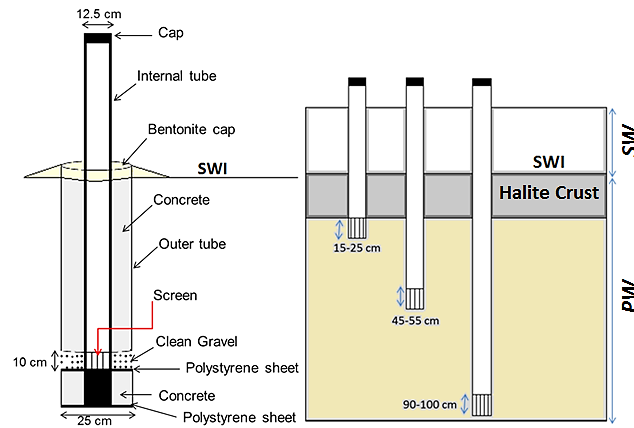
Fig. 2 Details of piezometers structures and sampling depths from pore water of Maharlu Lake (SWI: Sediment-Water Interface, SW: Surface Water and PW: Pore Water)
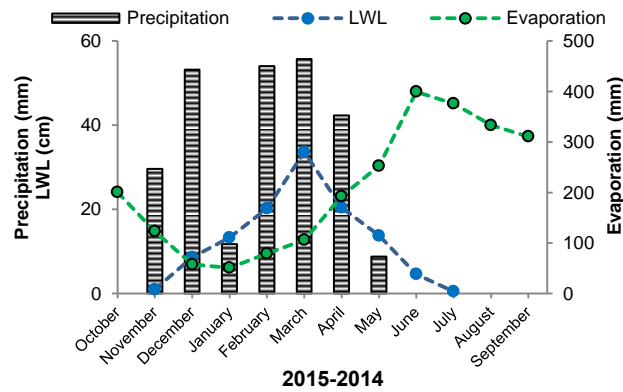

Fig. 3 Monthly variations of depths of precipitation and evaporation in Dobaneh Climatological Station and measured lake water level, LWL, (October 2014 to September 2015)

2.2. Climatological and Hydrological settings

Long-term (50-year) average of minimum and maximum recorded temperatures in the meteorological station of Dobaneh, located 2 km far from the Maharlu Lake to the north, are 9.0 ℃ and 25.2 ℃, respectively. Mean annual precipitation and potential evaporation in the area are 341 mm and 2572 mm, respectively. The fluctuations of Maharlu lake water level (LWL) are directly controlled by the interaction of evaporation and precipitation such that LWL increases in wet season with beginning precipitation (Fig. 3). Subsequently, LWL decreases in the dry season until the lake becomes completely dry due to lack of precipitation and a considerable increase in the evaporation rate. Generally, in playa lakes in which surface water is the dominant source of recharge, the playa surface is expected to become dry during dry seasons (Rosen 1994). Najmoddini and Raeisi (2011) reported

that Maharlu Lake water is mainly supplied from the basin runoff and direct precipitation on the lake surface. Groundwater level has declined throughout Maharlu Basin in recent years due to excess water extraction from the nearby aquifers (Kazemi et al. 2016). This provides preferred hydraulic conditions for brines intrusion from the lake to the adjacent aquifers (Jahanshahi and Zare 2016; Tajabadi et al. 2017). The major sources of recharge to Maharlu Lake are ephemeral rivers of Khoshk and Babahaji (Fig. 1) and direct runoff and direct precipitation on the lake area surface. The rivers originate from carbonate highlands in the northwest of the Maharlu Basin but receive significant inputs from urban, agricultural and industrial wastewater flowing through the basin to the lake.

3. Methodology

3.1. Sampling and Measurements

The water of the Babahaji River and the Khoshk River were sampled at two stations before their entrance to the Maharlu Lake (PF and EA sampling stations in Fig. 1). Four stations have been considered along the lake for sampling SW and PW of the lake with regular distances from the entry of the input rivers in the east of the lake (Fig. 1). To investigate the chemical variations at the sediment-water interface (SWI), three permanent piezometers were installed in each of these four stations to take PW samples from depths of 20, 50 and 100 cm. Details of the structure of the piezometers are illustrated in Fig. 2.

Lake water samples of SW and PW have been collected five times considering LWL fluctuations during one hydrological cycle (November 2014 to July 2015). The sampling time steps include: (1) before the inflow of freshwater to the lake in November 2014; (2) at the maximum water level in March 2015; (3) before complete dryness in July 2015; (4) and (5) in two intermediate periods in February 2015 and May 2015 (Fig. 3). All water and brine samples were filtered through 0.45 μm cellulose acetate membrane filters and collected in new acid-washed 60 ml polyethylene bottles. The brine samples collected for ICP-MS analysis were acidified to a pH <2 using ultrapure HNO_3.

Temperature and pH of the water samples were measured in the field during sampling. The concentration of sodium and potassium were measured by flame photometry (APHA 1998) in hydrochemical laboratory of Shiraz University. The concentration of calcium and magnesium were measured using titration with EDTA, Murexide and Erichrom Black-T as indicators (APHA 1998). Concentration of chloride and sulfate were measured using the Mohr chloride titration method and spectrophotometery, respectively (APHA 1998). Bicarbonate concentration was titrated with HCl and methyl orange as indicator (APHA 1998). Ion balances for all samples were calculated and deviations were found to be less than 5%. The concentrations of minor elements including Br, B and Li were analyzed using inductively coupled plasma- mass spectrometry (ICP-MS) (7700x, Agilent technologies) in the laboratory of the Institute of Geography at the University of Bern, Switzerland.

3.2. Numerical analysis

The data were not normally distributed. Correlations between the major and minor solute concentrations in SW and PW samples were calculated using the nonparametric spearman correlation. A p-value below 0.05 was considered to be significant. Principal component analysis which can indicate associations between samples and/or variables have been used frequently in hydrochemical investigations (e.g. Vega et al. 1998; Salifu et al. 2012; Zabala 2016). Principle component analysis (PCA) of the data was performed using the code IBM Statistic SPSS 22.0 for the whole 78 SW and PW samples. The hydrochemical data were standardized to zero mean and unit variance for avoiding of misclassification arising from different units of PCA constituents and variances. As the used method of classification here is nonparametric, we make no assumptions on statistical distribution of data and evaluation of normal distribution of them (Sharaf et al. 1986). Kaiser (1958) criterion of eigenvalues greater or equal to 1 was considered to determine the number of PCs from the PCA. The first PC which has the highest eigenvalue and accounts for the highest variance usually represents the most important controlling process (Salifu et al., 2012). The varimax orthogonal rotation was applied to

minimize the variances of the factor loadings across variables for each factor and facilitate the interpretation.

Calculations of mineral saturation indices, ionic strength and density were processed using the code PHREEQC for water samples (Parkhurst and Appelo 2013). Pitzer (1987) database which has been designed for highly mineralized water and brine samples was used for SW and PW samples. The chemical modeling simulating the evaporation of SW brines was performed with PHREEQC. Modeling was carried out at 25 ºC and 1 atm total pressure, for 1 kg of sample and in equilibrium mode where minerals are allowed to be precipitated and dissolved (in 24 steps to remove 54 mole of water). Equilibrium constants of the minerals are given in Table A1. The variations of the ion concentrations and saturation indices of the evaporite minerals during the evaporation were also investigated using PHREEQC.

4. Results and discussion

4.1. Chemical composition of input rivers and surface and pore water of the Maharlu Lake

The water types of the Babahaji River and Khoshk River are chloride-sulfate and chloride-bicarbonate, respectively (Table A2). The average values of EC (electrical conductivity) and TDS of rivers in their terminal points to the lake are less than 3 mS/cm and 2 g/l, respectively. The input rivers are saturated with respect to calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) but under saturated with respect to gypsum ($CaSO_4 \cdot 2H_2O$) and halite ($NaCl$) (Table A2). The average molar ratios of Na/Cl, Mg/Ca and Br/Cl in input rivers are 1.18, 1.10 and 6×10^{-4}, respectively (Table A2).

The hydrochemical water type of SW and PW samples is Na–Cl and the decreasing order of major cations is Na>Mg>K>>Ca and for the anions Cl>SO_4>>HCO_3 (Table 1 and 2). The values of TDS range from 150 to 389 g/l in SW samples and from 290 to 423 g/l in PW samples. The value of pH is in the neutral range between 6-8 (Table 1 and 2). Lake brines are saturated with respect to calcite and dolomite, mostly saturated with respect to gypsum and halite and mostly undersaturated with respect

Table 1 Physicochemical parameters, major ions and minor elements concentrations in SW samples of Maharlu Lake (see sampling stations in Fig. 1)

	Date	LWL (cm)	pH	IS	ρ	T (ºC)	Mg	Ca	SO$_4$	HCO$_3$	Cl	Na	K	TDS (g/L)	Error %	Li	B	Br
										(mMol/L)							(mg/L)	
Station 1	Nov.14	5	7.13	6.1	1.20	17.6	124	15	102	7.3	4050	4065	8.2	252	0.8	0.4	5.0	25.3
	Feb.15	42	8	6.7	1.21	15.3	175	10	84	5.0	4500	4185	13.8	276	-1.1	0.8	6.8	54.7
	Mar.15	38	7.6	8.8	1.26	18.4	213	17	89	5.5	5500	5043	16.1	328	1.5	1.0	8.9	64.3
	May.15	30	7.62	10.4	1.29	23.8	269	16	109	6.0	6050	5584	16.6	365	-0.8	-	-	-
	Jul.15	1	7.58	12.0	1.30	30.1	994	6	61	17.0	6250	4718	64.2	367	3.0	4.3	35.8	280.0
Station 2	Nov.14	1	7.51	3.3	1.11	15.4	168	6	42	4.4	2550	2196	9.2	151	-1.8	0.7	5.9	43.8
	Feb.15	25	7.84	8.2	1.25	15	195	10	63	4.3	5400	4739	13.2	314	-3.4	1.0	8.2	66.8
	Mar.15	33	7.69	9.7	1.28	16	269	11	104	5.4	5900	5217	19.2	355	2.7	1.3	10.2	81.7
	May.15	26	7.62	9.7	1.27	27.2	322	10	120	5.1	5700	5261	21.7	346	2.5	1.6	13.4	105.2
	Jul.15	1	7.08	-	-	42	1206	7	286	15.0	6200	4527	87.0	389	1.8	6.5	49.5	391.8
Station 3	Nov.14	1	7.54	8.5	1.25	18.7	210	9	55	5.0	5400	5109	16.9	324	0.3	1.0	8.1	70.5
	Feb.15	13	7.94	9.2	1.27	9.9	260	10	91	4.4	5500	5304	17.8	335	1.5	1.0	9.0	80.4
	Mar.15	21	7.66	11.1	1.31	18.4	276	14	359	3.9	5800	5457	20.2	376	3.7	1.1	10.3	83.3
	May.15	14	7.66	9.3	1.26	32.6	397	14	73	5.0	5650	4891	28.4	339	2.1	2.1	14.8	130.2
	Jul.15	1	6.88	13.8	1.32	50.1	1320	3	310	21.8	6200	4241	94.6	386	1.0	7.5	58.2	467.0
Station 4	Feb.15	1	7.77	6.6	1.21	12.4	233	27	61	2.9	4400	3957	102.5	270	0.6	1.2	6.3	76.9
	Mar.15	10.4	7.57	10.3	1.29	16.8	269	16	89	3.4	6200	5435	15.3	363	2.9	1.1	8.1	72.3
	May.15	1	7.17	11.9	1.29	31.3	1373	5	328	18.9	5500	3326	95.9	345	-1.4	-	-	-

LWL: Lake water level; IS: ionic strength (mol/kgw); ρ: density (g/cm^3), T: temperature; TDS: total dissolved solids

Table 2 Physicochemical parameters, major ions and minor elements concentrations in PW samples of Maharlu Lake (see sampling stations in Fig. 1)

	Date	Depth (cm)	pH	IS	ρ	T (°C)	Mg	Ca	SO$_4$	HCO$_3$	Cl	Na	K	TDS (g/L)	Error %	Li	B	Br
										(mMol/L)							(mg/L)	
Station 1	Nov.14	20	6.43	14.6	1.36	18.6	818	5	333	20.2	6500	5783	49.9	421	1.9	3.4	29.7	232.9
	Feb.15	20	7.29	9.8	1.28	18.6	475	13	161	9.8	5550	4848	29.9	339	-0.3	-	-	-
	Mar.15	20	7.01	9.0	1.26	15.3	258	17	99	5.0	5550	4978	16.9	336	1.8	1.2	9.3	74.3
	May.15	20	7.07	10.4	1.29	24.1	282	13	120	6.9	5950	5655	18.2	363	0.5	-	-	-
	Jul.15	20	7.03	12.0	1.31	31.9	612	3	148	12.3	6250	5553	43.0	385	2.0	3.0	23.4	195.3
	Nov.14	50	6.14	9.6	1.27	19.4	512	5	177	12.2	5250	4804	37.1	332	2.2	2.4	15.0	177.4
	Feb.15	50	7.06	10.4	1.28	17.9	616	9	193	11.6	5600	4717	37.1	345	0.1	-	-	-
	Mar.15	50	7.01	10.4	1.29	14.4	423	10	156	8.5	5950	5109	28.4	357	2.2	2.1	16.1	136.6
	May.15	50	6.99	10.4	1.29	24.2	297	15	125	7.8	5850	5703	20.7	368	1.9	-	-	-
	Jul.15	50	6.88	11.9	1.30	31.8	880	3	150	18.0	6050	4909	57.5	368	2.8	3.7	29.8	239.5
	Nov.14	100	6.6	10.8	1.29	19.6	699	6	203	3.2	5600	4804	42.2	349	1.9	2.7	14.8	198.6
	Feb.15	100	7.06	10.3	1.28	16.6	427	11	156	7.4	5900	5000	28.1	360	-2.6	-	-	-
	Mar.15	100	7.06	9.4	1.27	16.6	288	8	125	5.1	5700	5043	20.7	340	2.6	1.3	9.7	85.7
	May.15	100	7.04	10.4	1.29	24.4	285	10	115	6.3	5800	5822	19.7	363	3.2	-	-	-
	Jul.15	100	6.77	12.3	1.32	30.6	505	5	236	7.1	6400	5506	73.4	396	-2.1	1.9	11.5	146.3
Station 2	Nov.14	20	7.43	8.7	1.24	17.2	806	3	234	13.4	4750	3370	48.6	292	-2.0	0.7	43.9	329.6
	Feb.15	20	7.75	9.8	1.28	13.8	519	6	188	8.5	5550	4630	34.5	337	-1.9	-	-	-
	Mar.15	20	7.48	9.8	1.28	16.2	419	6	161	8.5	5700	4848	35.5	349	2.5	1.1	76.9	649.2
	May.15	20	7.23	9.9	1.27	26	579	9	177	10.1	5500	4609	36.1	336	2.3	-	-	-
	Jul.15	20	7.11	13.1	1.31	34.9	1432	3	259	17.9	5800	4050	92.1	367	5.1	0.9	60.5	470.9
	Nov.14	50	6.91	11.7	1.29	15.2	1436	8	344	21.5	5300	3130	92.3	336	0.7	0.9	60.5	472.0
	Feb.15	50	7.15	12.2	1.30	11.4	1463	2	297	19.8	5550	3391	97.2	345	2.0	-	-	-
	Mar.15	50	6.99	13.2	1.32	16.4	1485	6	339	21.1	5800	3587	107.4	364	-1.4	0.8	50.3	399.4
	May.15	50	7.03	11.0	1.28	25.5	1023	7	255	15.8	5550	3848	65.0	346	1.8	-	-	-
	Jul.15	50	6.69	13.8	1.33	33.2	1232	3	331	20.0	6100	4527	85.7	389	2.2	0.8	55.8	452.3
	Nov.14	100	6.93	11.6	1.29	17.2	1449	5	313	21.1	5250	3152	98.7	330	2.1	0.9	58.2	472.4
	Feb.15	100	7.16	13.1	1.32	11.6	1558	3	313	18.1	5750	3522	102.3	366	2.7	-	-	-
	Mar.15	100	7.01	12.6	1.31	16.5	1479	5	339	21.4	5500	3565	104.9	353	-3.4	0.9	60.9	501.6
	May.15	100	6.87	12.0	1.29	24.1	1429	6	323	22.1	5550	3152	93.4	344	2.8	-	-	-
	Jul.15	100	7.06	13.1	1.32	33.6	1265	3	231	18.3	6100	4313	89.5	376	2.6	0.7	57.1	462.6

Abbreviations are similar to Table 1

Table 2 continued

	Date	Depth (cm)	pH	IS	ρ	T (ºC)	Mg	Ca	SO₄	HCO₃	Cl	Na	K	TDS (g/L)	Error %	Li	B	Br
										(mMol/L)				(g/L)	%		(mg/L)	
Station 3	Nov.14	20	7.49	10.5	1.28	17.9	769	12	161	8.3	5500	4565	52.6	338	2.7	-	-	-
	Feb.15	20	7.63	12.6	1.31	8.9	1488	2	333	15.8	5500	3565	102.3	350	3.6	-	-	-
	Mar.15	20	7.71	10.1	1.28	15.2	562	8	130	7.5	5650	4826	37.6	348	-0.7	-	-	-
	May.15	20	7.55	10.5	1.28	26.3	624	11	198	7.9	5700	4696	41.2	349	2.8	-	-	-
	Jul.15	20	7.25	13.7	1.33	35.9	1226	4	323	19.5	6250	4336	92.1	391	-0.2	-	-	-
	Nov.14	50	7.1	12.5	1.31	15.8	1402	7	313	18.4	5750	3500	102.6	356	0.1	-	-	-
	Feb.15	50	7.5	12.6	1.31	10.3	1398	2	333	15.0	5500	3783	106.1	353	3.9	-	-	-
	Mar.15	50	7.26	12.4	1.30	14.7	1708	4	224	20.1	5750	2870	117.6	340	-1.5	-	-	-
	May.15	50	7	12.4	1.30	24.5	1382	6	313	17.0	5750	3478	90.8	360	4.1	-	-	-
	Jul.15	50	6.96	14.1	1.33	35.6	1478	4	378	21.6	6100	3811	99.7	383	0.0	-	-	-
	Nov.14	100	6.15	12.5	1.30	19	1574	5	344	13.8	5500	3109	110.3	343	1.3	-	-	-
	Feb.15	100	6.39	11.6	1.29	11.8	1333	1	349	9.3	5300	3326	115.1	342	0.8	-	-	-
	Mar.15	100	7.38	12.4	1.31	15.4	1339	7	318	8.8	5500	3870	88.2	353	-3.9	-	-	-
	May.15	100	6.49	12.8	1.30	23	1596	4	354	10.3	5650	3065	106.1	352	2.1	-	-	-
	Jul.15	100	6.65	14.6	1.33	30.2	1710	2	408	9.6	6100	3430	111.3	384	0.3	-	-	-
Station 4	Nov.14	20	7.09	11.4	1.28	18.2	1474	8	365	17.8	5100	2870	112.8	325	0.7	8.6	65.5	541.0
	Feb.15	20	7.2	13.0	1.31	8.7	1771	4	359	16.0	5550	2848	103.8	346	1.7	-	-	-
	Mar.15	20	7.25	12.9	1.30	13.7	1797	3	359	17.3	5500	2717	113.8	349	-1.5	8.4	64.6	520.3
	May.15	20	7	12.7	1.30	27.9	1594	6	354	15.4	5650	3065	90.8	350	0.6	-	-	-
	Jul.15	20	6.72	15.7	1.35	33.5	1856	1	544	20.6	6100	3263	112.5	398	-0.8	9.4	69.0	560.2
	Nov.14	50	6.63	13.2	1.31	15.3	1874	4	495	21.4	5150	2652	121.8	346	2.9	9.2	55.8	579.1
	Feb.15	50	7.07	13.6	1.32	9.5	1812	3	359	13.6	5700	3043	111.3	357	2.7	-	-	-
	Mar.15	50	7.09	13.2	1.31	14.2	1838	8	354	15.9	5600	2783	117.6	348	-2.1	9.3	65.0	555.0
	May.15	50	6.89	12.6	1.30	25	1532	6	328	16.6	5700	3152	89.5	356	-0.5	-	-	-
	Jul.15	50	6.75	17.2	1.37	35.1	1777	4	646	19.4	6300	3788	116.4	423	-1.0	7.7	58.9	500.0
	Nov.14	100	6.4	11.9	1.30	18	1062	5	297	11.0	5750	4087	88.5	358	-0.4	6.0	28.2	403.5
	Feb.15	100	7.14	13.0	1.31	9.7	1764	1	328	12.6	5600	2957	103.8	353	2.5	-	-	-
	Mar.15	100	7	14.1	1.32	14.7	1939	3	354	14.5	5900	2848	108.7	363	-1.6	8.9	62.9	526.2
	May.15	100	7.06	12.1	1.30	22.9	1369	6	333	12.5	5600	3391	67.8	349	-0.7	-	-	-
	Jul.15	100	6.66	16.0	1.35	33.7	1692	3	603	18.4	6300	3406	110.0	410	-4.3	8.2	61.7	524.7

Abbreviations are similar to Table 1

to sulfates and chlorides of K and Mg such as epsomite ($MgSO_4 \cdot 7H_2O$) (Table A3 and A4). The Na/Cl molar ratio in the lake brines ranges from 0.48 to 1.00, the Mg/Ca molar ratio ranges from 8 to 1764 and the Br/Cl varies between 7.8×10^{-4} to 1.4×10^{-3} (Table A3 and A4). The chemical composition and average salinity of the surface brines of Maharlu Lake are similar to shallow Eyre Lake in the Northern South Australia (Johnson 1980). But the average Na/Cl molar ratio in Mahahlu Lake (0.86) is less than Eyre Lake (0.94). The salinity of SW in station 1 of Maharlu Lake is on average 172.6 times more concentrated than its input rivers, and all major and minor solutes, except Ca and HCO_3, are enriched intensively in lake brines (Table A5).

4.2. Brine evaporative evolution of surface and pore water

The evaporative evolution of brines generally exerts an important control on major and minor solutes behavior in saline systems. Evaluating the behavior of conservative solutes during brine evaporation has been suggested to characterize the degree of evaporation (Deocampo and Jones 2013). The elements Br, K and Mg behave conservatively in Na-Cl brines that are supersaturated with respect to halite whereas they are undersaturated with respect to sulfates and chlorides of K and Mg (Eugster and Jones 1979). The SW and PW of the Maharlu Lake have similar geochemical characteristics. Cl shows a strong positive correlation with TDS, but no correlation with Na (Fig. 4a-b). Br shows no significant correlation with Cl (Fig. 4c) while it has a strong positive correlation with Mg (Fig. 4d). TDS slightly increases with increasing Mg concentrations (Fig. 4l). Mg shows negative correlations with Na and Ca, but positive correlations with SO_4 and HCO_3. Strong positive correlations with Mg are observed for K (Fig. 4g) and B (Fig. 4j). Li generally shows a positive correlation with Mg although it is likely to precipitate in station 2 where it has very low concentrations (Table 1 and 2). Therefore, Li does not behave as a conservative solute in the brines (Fig. 4k).

Eugster and Jones (1979) proposed a chemical model for extreme evaporation of closed basin brines in which three different types of chemical behavior for major and minor solutes are expected during brine evaporative evolution (Fig. 5a). According to their proposed model, solutes type I include those solutes that behave conservatively. They do not participate in mineral precipitation or absorption

mechanisms, and their concentrations linearly increase as the degree of evaporation increases. Type II includes cation-anion pairs (IIa and IIb in Fig. 5a) which participate together in precipitation of evaporitic minerals. Concentrations of both ions increase first as evaporation proceeds. Then as mineral precipitation begins, these solutes experience a stage of constant concentrations as brine evaporation progresses. With additional mineral precipitation, the solute which had the lower initial concentration (IIb in Fig. 5a) will be depleted in the brine while a surplus of the other ion (IIa in Fig. 5a) concentrates in the brine as the degree of brine evaporation increases.
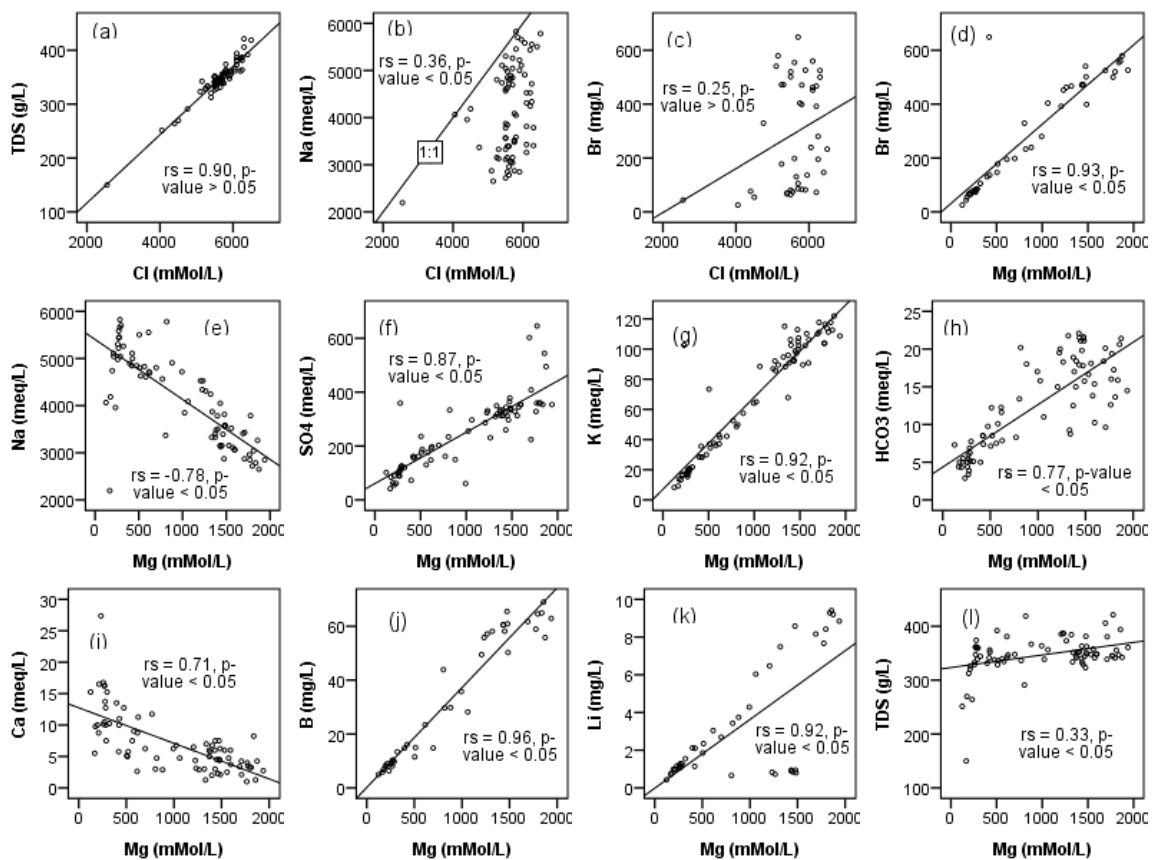
Fig. 4 Spearman correlations coefficients (rs) between TDS and Cl (a), Cl and Na (b), Br and Cl (c), Br and Mg (d), Na and Mg (e), SO4 and Mg (f), K and Mg (g), HCO3 and Mg (h), Ca and Mg (i), B and Mg (j), Li and Mg (k) and TDS and Mg (l) in total SW and PW brines of the Maharlu Lake (p-value less than 0.05 consider significant correlation and lines are fitted to total points by SPSS)

Chemical modeling is useful to investigate the variations of major ions during evaporative evolution of salt lakes and it has been used extensively in previous studies (Herczeg and Berry Lyons 1991; Wahed et al. 2015; Kolpakova and Gaskova 2017). In order to evaluate if solute behavior of the

Maharlu brine during an evaporation cycle is compatible with the Eugster and Jones (1979) model, geochemical modeling was performed using the PHRQPITZ code (Fig. 5).
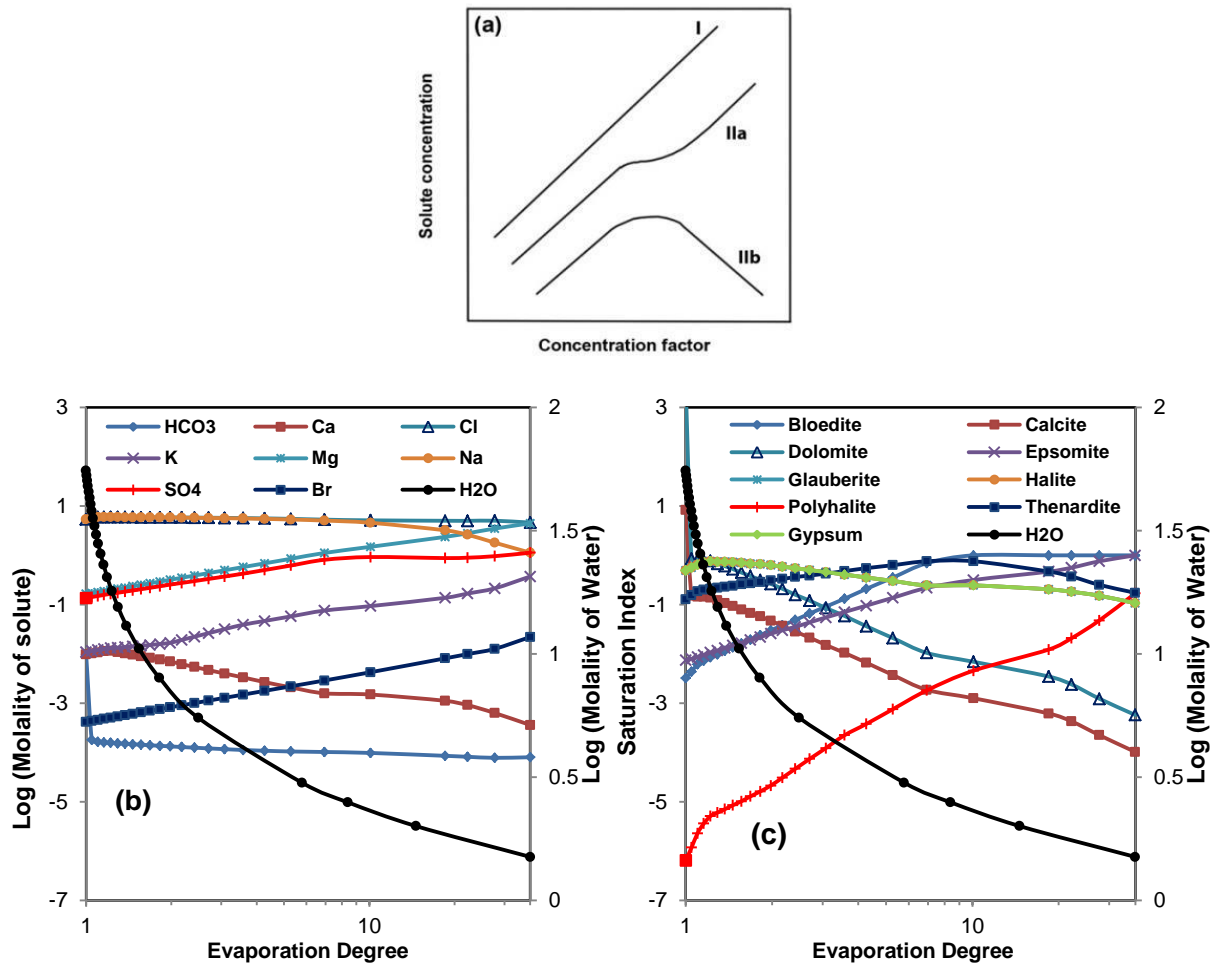

Fig. 5 a) Schematic results of solutes model for evaporation of closed-basin brines proposed by Eugster and Jones (1979); **b**) results of simulation of major and minor solutes concentrations; **c**) the saturation indices of evaporite minerals variations in evaporating SW brines

The SW samples collected in November from the entry point of the lake with the least degree of evaporation (least K and Mg concentration) were considered as input water to the model. In the evaporation model, concentrations of Br, K and Mg rise continuously as the degree of evaporation increases (Fig. 5b); i.e. these solutes behave conservatively and are characterized as solutes of type I (Fig. 5a). In contrast, Ca, Cl, HCO$_3$, Na and SO$_4$ participate in precipitation of carbonates, sulfates and chlorides (Fig. 5c). Among them, Ca and Na show declining concentrations after an initial early

evaporation stage (Fig. 5b). Therefore, Ca and Na behave as the solutes type IIb of the Eugster and Jones's model (Fig. 5a).

The modeling suggests that when the primary SW is concentrated several times by evaporation, chemical composition of PW brine at station 4 (the most concentrated brine sample in the lake) is obtained. The results of the model show that brine samples of the lake are expected to become undersaturated with respect to calcite, dolomite, gypsum and glauberite as evaporation proceed (Fig. 5c). However, the values of saturation indices of these phases which have been calculated based on measured chemical compositions of SW and PW samples are much higher than the predicted values by modeling (see the Table A3 and A4). This suggests that evaporation is not the only controls of chemical composition of lake brines. Other likely factors affecting chemical composition of lake brine include dissolution-precipitation reactions, chemical interaction with pore water and ion exchange with lake sediments. Role of these processes will be discussed later in section 4.4.

4.3. Hydrochemical evidences of interaction between surface and pore water

Hydrochemical interactions of SW and PW across the sediment-water interface are an important controls on the chemistry of salt lakes (Lerman and Jones 1973; Spencer et al. 1985; Torgersen et al. 1986; Anderson et al. 2014). Distribution of SW and PW samples of Maharlu Lake on the ternary diagrams of Na-SO_4-Mg and K-HCO_3-Ca suggests mixing-like trends between SW and PW samples in a number of stations (indicated as arrows on Fig. 6). Mixing of PW samples with SW samples generally results in lowering the relative concentrations of K and Mg but increasing the relative concentrations of Ca and Na in PW brines.

The vertical profile of Br/Cl ratio has been suggested as a useful indicator to investigate the interaction between SW and PW brines in saline lakes (Anderson et al. 2014). In station 1, Br/Cl ratio decreases in PW samples of different depths with increasing LWL in March 2015 whereas it increases in SW at the same time (Fig. 7). Br/Cl ratio increases in PW with LWL reduction at the end of study period whereas it decreases in SW (Jul. 2015). This suggests a significant interaction between PW-SW in station 1 such that Br is exchanged between PW and SW with rising LWL during the study

period. This is a common phenomenon at the mouth of the freshwater rivers entering the salt lake such that the chemical composition of PW is typically similar to SW of the lake due to dilution with freshwater (Lerman and Jones 1973).
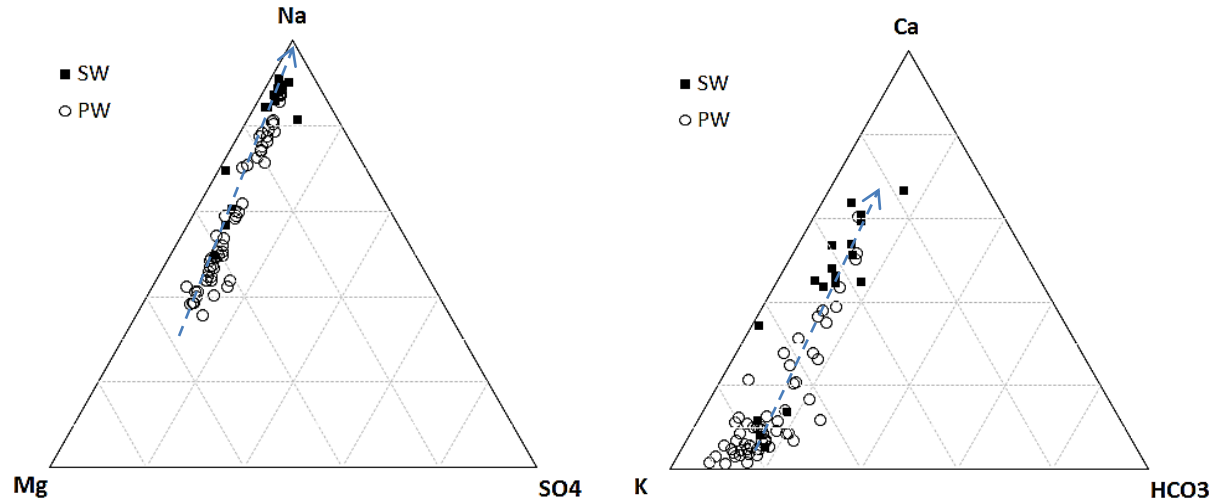

Fig. 6 Distribution of SW and PW brines samples on ternary diagram of Na-SO$_4$-Mg (a) and K-HCO$_3$-Ca (b) (concentrations in meq/l)
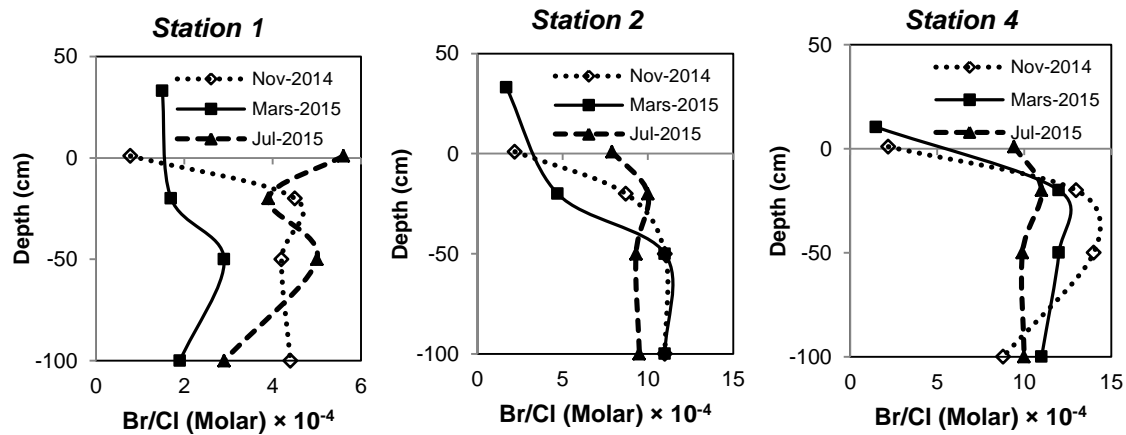

Fig. 7 Vertical profile of Br/Cl molar ratio across SWI in three stations as a function of distance from input rivers (create by excel 2010)

Vertical distribution of the Br/Cl ratio in station 2 indicates that the interaction between SW and PW occurs only until a depth of 20 cm in March 2015. No exchange or interaction is observed in deeper sections at station 2. There is a significant difference between Br/Cl ratios in SW and PW brines at station 4 throughout the study period (Fig. 7). This indicates a negligible interaction between SW and PW in station 4 due to LWL fluctuations. It has been already reported that the hydrochemical interactions between SW and shallow PW are limited due to presence of evaporite impermeable layers

(Anderson et al. 2014). As a result, SW and PW are in interaction with increasing the LWL but the depths of SW and PW interaction decreases with distance from the input rivers.

4.4. Major controls on chemical composition of surface and pore water

The chemical modeling of SW evaporation indicated us that evaporation is not the only chemical control of the Maharlu brines. For investigation of the major controls on chemical composition of the lake, a principal component analysis (PCA) was applied to all 78 SW and PW brine samples. The analysis reduced the dimensionality of 14 physicochemical parameters to three principal components (PCs) which explain 85.8% of variance in the dataset. Loading values greater than +0.5 and lower than -0.5 have been considered significant (Table 3).

Table 3 Varimax loading of the physicochemical variables for each principal component

	PC1	*PC2*	*PC3*
Mg	**0.87**	0.17	-0.04
Ca	**-0.63**	-0.12	**0.16**
Cl	0.02	**0.96**	0.04
Na	**-0.88**	0.41	0.12
K	**0.90**	0.16	-0.14
TDS	0.16	**0.97**	0.00
Na/Cl	**-0.97**	-0.06	0.07
SI-Calcite	**-0.66**	-0.28	**0.68**
SI-Gypsum	0.19	**0.49**	**0.71**
SI-Halite	0.05	**0.86**	-0.04
SI-Dolomite	-0.21	0.02	**0.86**
SI-Glauberite	0.34	**0.88**	0.23
SI-Epsomite	**0.78**	0.58	0.15
SI-Polyhalite	**0.91**	**0.30**	0.06
% Variance explained	41.33	31.19	13.30
Cum. % var. explained	41.33	72.52	85.81

SI: saturation index

The first principal component (PC1) shows high positive loadings for K, HCO_3, Mg, SO_4, and the saturation indices of epsomite, polyhalite, and significant negative loadings for Ca, Na, Na/Cl and the saturation index of calcite (Table 3). As discussed in section 4.2, the concentrations of K and Mg (typically conservative) increase while Ca and Na decrease due to evaporation. It can be concluded that PC1 is the *evaporation factor* which explains about 41% of variance in the dataset (Table 3). Chemical fractionation of the solutes due to precipitation of evaporite minerals changes the chemistry of salt lakes (Eugster and Jones 1979). Significant alterations typically occur in chloride lakes

according to a sequence of mineral precipitation (Eugster and Jones 1979; Kolpakova and Gaskova 2017). For example carbonate and gypsum precipitation at the primary stage of evaporative evolution of Na-Cl brines can deplete the brines from Ca and increase the Mg/Ca ratio (Deocampo and Jones 2013).

The second principal component (PC2) shows high positive loadings for Cl, TDS and saturation indices of glauberite and halite, and significant positive loadings for saturation indices of gypsum and polyhalite (Table 3). Saturation index of polyhalite in the brine samples ranges from unsaturated to supersaturated (Table A3 and A4) and is controlled by both PC1 and PC2 (Table 3). In addition, lake brine samples are supersaturated with respect to glauberite, halite and gypsum (Table A3 and A4). These saturation indices increase along the lake axis due to their dissolution at the entry point of rivers and increasing degree of evaporation in farther stations (Fig. 10). Decrease of the saturation indices might occur due to the precipitation of pertinent mineral phases. Therefore, it can be concluded that PC2 is a *dissolution-precipitation factor* of highly soluble minerals. The selective dissolution of efflorescent crust (Eugster and Jones 1979) can be another name for this factor which explains about 31% of the variance in the dataset. This process has little effect on major ion ratios but has an important role on minor element compositions of the resultant brines in sodium chloride lakes (Herczeg and Lyons 1991). However, high TDS loading in this component suggests that the salinity of brines is mainly controlled by the PC2 (Table 3).

The third principal component, PC3, shows high positive loadings for Ca concentration and saturation indices of calcite, dolomite and gypsum. Dolomite is formed in salt lakes due to dolomitization of carbonates by Mg enriched waters (Warren 2000). This secondary carbonate is only found in lake sediment with high-magnesium calcite and a Mg/Ca ratio >7 and a ratio >40 converts dolomite to huntite or magnesite (Müller et al. 1972). The minerals of dolomite, huntite and magnesite are present in the Maharlu Lake sediments (Khosravi, 2018). The Mg/Ca molar ratio ranges from 15 to 1764 in PW of Maharlu Lake which varies significantly with LWL fluctuations (Table A3 and A4). Transformation between dolomite, huntite and magnesite occur in shallow salt lakes (such as shallow Tuz Gölü Lake in Turkey) due to Mg/Ca variations with LWL fluctuations (Müller et al. 1972). The process of dedolomitization might occur in dolomite-calcite equilibrated waters due to calcium

enrichment by gypsum dissolution. As a result of dedolomitization, dolomite is typically dissolved and replaced by secondary sulfate and by calcite in primary evaporites (Peryt and Kasprzyk 1992). This leads to an increase of concentrations of Mg, SO_4, and Ca in the remaining water (Appelo and Postma 2005). Therefore, the third principal component (PC3) of analysis generally consistent with the process of diagenetic evolution of carbonates which explains about 13% of the data variances (Table 3). SI-Calcite and Ca concentration are additionally controlled by the evaporation factor (PC1, Table 3). Negative scores of these parameters in PC1 are considered to be the consequence of calcite precipitation as evaporation proceeds. The study of the PC3, which is one of the more complicated diagenetic processes in salt lakes, needs more detailed sedimentology and hydrochemistry investigations and is beyond the scope of this research..

4.5. Spatial and seasonal variations in chemical composition of surface and pore water

No specific trend is observed in the values of density, ionic strength, pH, TDS, and Cl concentration with distance from the input rivers (Fig. 8a-e). The values of density and ionic strength increase with depth at all stations whereas pH value decreases with depth (Fig. 8b-d). The factor of *dissolution-precipitation* of highly soluble minerals (PC2) controls the Cl concentration and TDS values in SW and PW of lake. This factor can also control other salinity-dependent parameters such as density and ionic strength. Increasing concentrations/values of these parameters with depth indicates the role of *dissolution-precipitation* of highly soluble minerals (PC2) increases with depth. PW in playa lakes shows usually more salinity than SW due to this mechanism (Jones et al. 1969).

In PW of the lake, Br, Mg and SO_4 concentration and Br/Cl and Mg/Ca increases with distance from the input rivers whereas concentration of Ca and Na and the ratio of Na/Cl decreases with distance (Fig. 8f-j and 9). However, these parameters show no significant changes with distance from input rivers in SW samples of the lake. While Mg concentration and Mg/Ca increases with depth in stations 2 and 3, a decreasing trend of Na concentration and Na/Cl with depth is observed in these stations (Fig. 8 and 9). However, no distinct trend is observed in concentrations of Mg and Na and Mg/Ca and Na/Cl with depth in stations 1 and 4 (Fig. 8 and 9). As mentioned in section 4.4, factor of *evaporation* (PC1) controls most of these parameters in SW and PW of the lake. Considering the variation trend of
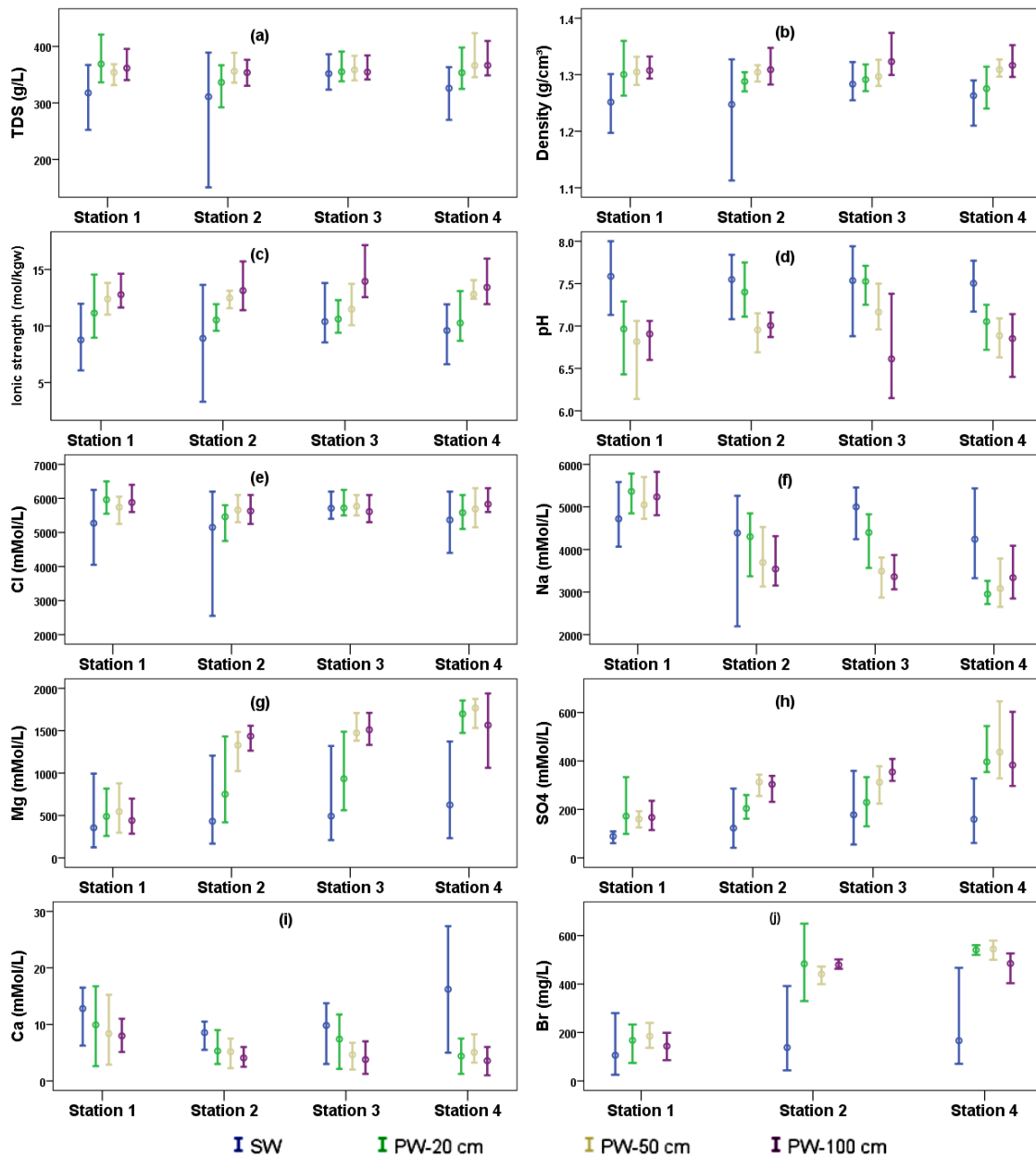
Fig. 8 Spatial and vertical variations of physiochemical parameters in SW and PW brines of the Maharlu Lake; each bar shows the minimum, average and maximum values of the parameters in special depths of the sampling stations during the study period

these parameters, it can be concluded that the evaporation degree of PW increases with distance from input rivers and with depth in station 2 and 3. While the evaporation degree of SW shows no significant variations with distance from input rivers, this suggests that the interaction between SW and PW across sediment water interface of sampling stations controls the variations of brine evaporation degree with depth. As discussed in section 4.3, significant interaction between PW and SW occurs in station 1 with LWL fluctuations. SW and PW in station 1 show similar values of

parameters which are controlled mostly by evaporation degree of brine in the lake (including the Mg and Na concentrations and Br/Cl, Mg/Ca and Na/Cl). The interaction between SW and PW in station 2 and 3 is limited to shallow depths that results in a decreasing evaporation degree at these stations. Unlike station 1, negligible interaction between SW and PW in station 4 resulted in high differences for the parameters controlled mostly by evaporation.
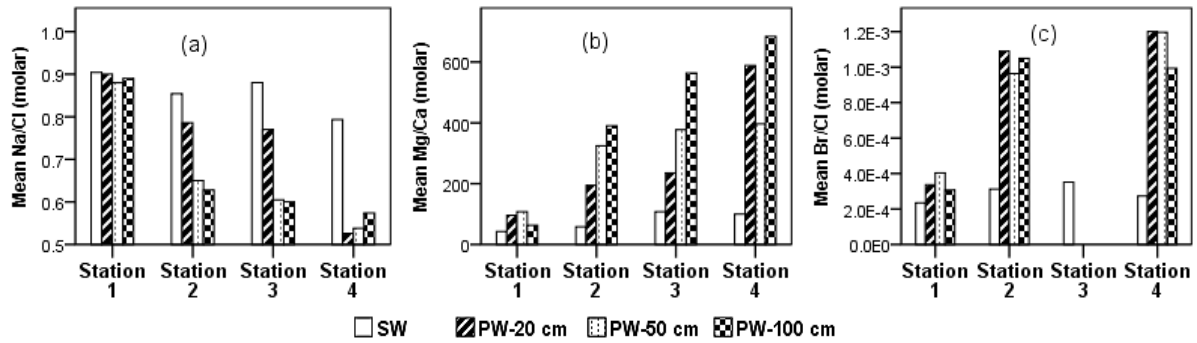
Fig. 9 Mean values of molar ratios of (a) Na/Cl, (b) Mg/Ca and (c) Br/Cl in SW and PW brines of Maharlu Lake as a function of distance from input rivers, depth
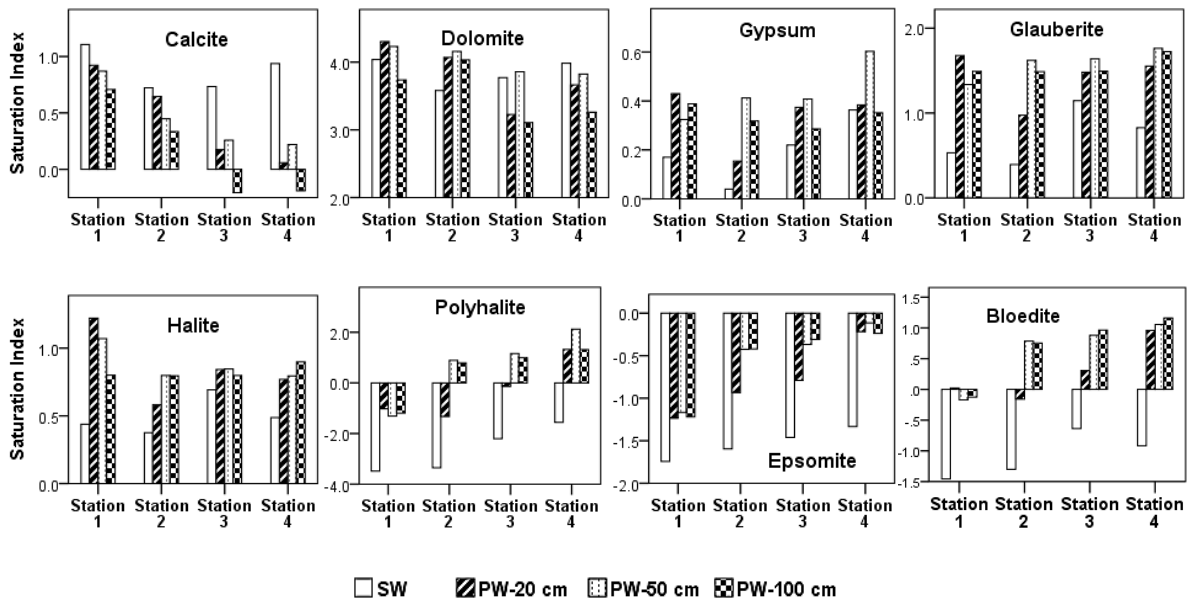
Fig. 10 Mean saturation indices of evaporite minerals in SW and PW brines of Maharlu Lake as a function of distance from input rivers and depth

No trend could be distinguished with distance from the input rivers in the saturation indices (SI) of bischofite, calcite, dolomite, epsomite, gypsum, halite and polyhalite in the SW samples (Fig. 10). Otherwise, a variety of trends are observed in the saturation indices of PW samples. The saturation

index of calcite in PW samples generally decreases with distance from input rivers and with increasing depth. Saturation indices of those phases that are present in lake bed sediments including dolomite, gypsum, halite and glauberite, show a quick increase in station 1 due to dissolution (Fig. 10). No distinct trend with distance from the input rivers is observed beyond station 1 (Fig. 10). Saturation indices of bloedite, epsomite and polyhalite, i.e. those phases that the brine samples are undersaturated to saturated with respect to them, continuously increase with distance from input rivers (Fig. 10).

The changes of saturation indices of bloedite, calcite, epsomite and polyhalite suggest that the evaporation degree of PW increase with distance from input rivers. However, no distinguished trend is observed in the saturation indices of the mentioned minerals with depth at four stations (Fig. 10).

The water level increases in wet seasons as precipitation begins (typically in November) and decreases in dry seasons until the lake becomes completely dry, typically in July (Fig. 3). The fluctuations of LWL decrease with distance from the input rivers (Table 1) and the LWL fluctuations at station 4 (the farthest away station from input rivers) occurs over a shorter time period than at the other stations (Table 1). As a result, the interaction between SW and PW reduces with distance from input rivers as LWL fluctuations decreases.

The concentrations of Br, Cl, Mg, Na and TDS in the SW samples indicate a general increasing trend with time during the study period (Fig. 11). However, Na concentration decreases at the end of the period after that general increasing trend. It seems that the evaporation degree of SW increases continuously during the LWL fluctuation period due to evaporation and interaction with PW.

Cl concentration and TDS values of PW brine samples show slight seasonal variations during the study period (Fig. 11). The Na behavior in PW brines of station 1 is similar to that of SW brine samples of the lake; i.e. an initial increasing trend, which gradually becomes a decreasing trend at the end of the period. Concentration of Na increases at station 2 and remains constant at station 3 during the study period. The concentrations of Br, Mg and SO4 in PW brines of station 1 show a general inverse behavior with LWL fluctuations i.e. they decrease with rising LWL and subsequently increase with falling LWL (Fig. 11).
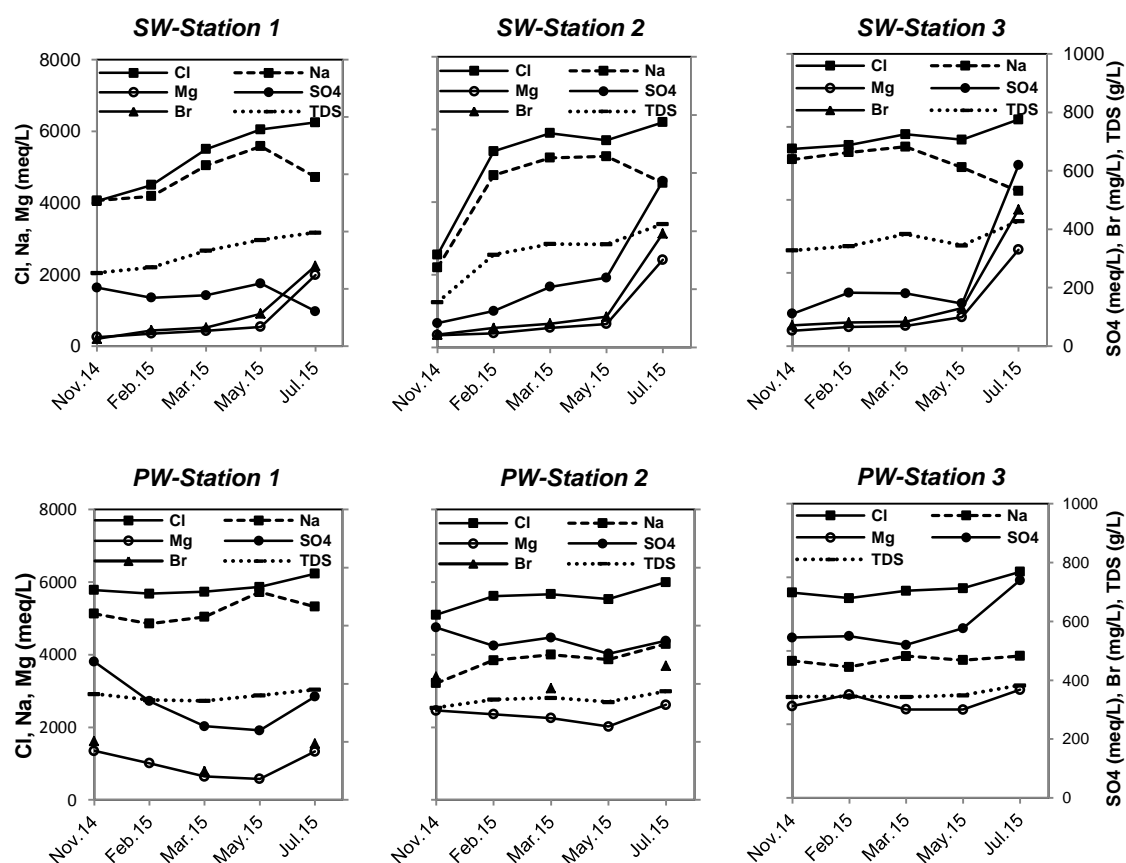
Fig. 11 Concentration of Major and minor solutes and TDS values during a complete LWL fluctuations period in SW and PW brines (Nov.2014-Jul.2015)

5. Conclusions

Our investigations suggest that chemical interaction occurs between surface water and shallow pore water of the Maharlu Lake. Generally, in comparison to surface water, pore water samples of the lake show a higher degree of evaporation, higher concentrations of B, Br, K, Mg and Br/Cl and Mg/Na ratios, and lower amounts of Ca and Na and Na/Cl ratio. Degree of evaporation increases with distance from inflowing point of the rivers to the lake in PW samples while it shows no significant spatial variation in SW. The surface water of the Maharlu Lake shows significant seasonal variations with fluctuations in the lake water level which affects the physical and chemical properties of the shallow pore water beneath the lake in turn. The interaction between surface and pore water of the lake causes a decrease in the degree of evaporation of the sediment pore water. The degree of connectivity between surface water and pore water of the Maharlu lake is a function of distance from

the input rivers, and it decreases with increasing distance from the input rivers and also with increasing depth.

Our hydrochemical and statistical investigations indicate that evaporation degree and dissolution-precipitation of high soluble minerals in lake bed sediments are the major processes governing chemical composition of surface and pore brine of Maharlu lake. Additionally, the process of dolomite diagenesis (dolomitization-dedolomitisation) is considered as a minor factor influencing chemical composition of pore water of Maharlu Lake.

As a conclusion, the physicochemical parameters and chemical composition of surface water and shallow pore water in seasonal salt lakes such as Maharlu have considerable vertical, seasonal and spatial variations. Temporal variations are mainly due to lake water level fluctuations while spatial and vertical variations are functions of distance from input rivers. These variations should be considered in studies of geochemical and biological processes, the interaction between surface and pore water and surrounding groundwater resources, and in term of characterizing distribution and fate of contaminants in water and sediments of the lakes.

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Appendices

Table A1 Equilibrium phases considered in the simulation of evaporation processes

Mineral	Chemical formula	Log k 25 ºC
Anhydrite	$CaSO_4$	-4.36
Aragonite	$CaCO_3$	-8.33
Bischofite	$MgCl_2:6H_2O$	4.45
Bloedite	$Na_2Mg(SO_4)_2:4H_2O$	-2.35
Calcite	$CaCO_3$	-8.41
Carnallite	$KMgCl_3:6H_2O$	4.33
Dolomite	$CaMg(CO_3)_2$	-17.08
Epsomite	$MgSO_4:7H_2O$	-1.88
Glauberite	$Na_2Ca(SO_4)_2$	-5.25
Gypsum	$CaSO_4:2H_2O$	-4.58
Halite	$NaCl$	1.57
Hexahydrite	$MgSO_4:6H_2O$	-1.63
Kainite	$KMgClSO_4:3H_2O$	-0.19
Polyhalite	$K_2MgCa_2(SO_4)_4:2H_2O$	-13.74
Thenardite	Na_2SO_4	-0.35

Table A2 The average of physicochemical parameters of input Babahaji and Khoshk Rivers (November 2014-July 2015)

Parameter	Babahaji River	Khoshk River	Mean
TV* (Mm^3)	21.0	15.6	-
pH	7.13	7.99	7.33
Eh (V)	-0.016	+0.183	+0.069
T (ºC)	21.1	22.4	21.6
EC (mS/cm^2)	2.5	2.1	2.4
Density (g/cm^3)	0.998	0.998	0.998
Ionic Strength (mol/kgw)	0.036	0.037	0.36
Mg (mMol/l)	3.8	4.5	4.1
Ca (mMol/l)	3.8	3.7	3.8
SO_4 (mMol/l)	2.0	4.5	3.1
HCO_3 (mMol/l)	12.8	6.2	10.0
Cl (mMol/l)	9.9	8.7	9.4
Na (mMol/l)	10.4	7.8	9.3
K (mMol/l)	0.44	0.50	0.47
TDS (g/l)	1.9	1.7	1.8
Br (µg/l)	304.4	327.6	314.3
B (µg/l)	475.8	462.5	470.1
Li (µg/l)	26.5	31.3	28.5
Na/Cl (molar)	1.38	0.91	1.18
Mg/Ca (molar)	0.98	1.25	1.10
Br/Cl (molar)	0.0007	0.0005	0.0006
SI-Calcite	0.6	1.1	0.8
SI-Dolomite	1.4	2.4	1.8
SI-Gypsum	-1.3	-0.9	-1.2
SI-Halite	-6.0	-5.9	-6.0

TV*: Total Volume which is drained to the lake through the input rivers during the study period. Mean of two rivers parameters (except pH) is calculated with considering the volume of water which is drained to the lake through the each river; SI: saturation index

Table A3 Na/Cl, Mg/Ca, Li/Cl, Br/Cl and B/Cl molar ratios and mineral saturation indices in SW samples of Maharlu Lake (see sampling stations in Fig. 1)

	Date	Na/Cl	Mg/Ca	Li/Cl	Br/Cl	B/Cl	Saturation Indices							
				(Molar)			CA	DO	GY	BL	EP	GL	PO	HA
Station 1	Nov.14	1.00	8	1.5E-05	7.8E-05	1.2E-04	1.16	3.54	0.02	-2.51	-2.05	-0.3	-5.6	-0.15
	Feb.15	0.93	18	2.5E-05	1.5E-04	1.5E-04	1.32	4.23	-0.13	-2.28	-1.88	-0.39	-5.2	0.01
	Mr.15	0.92	13	2.5E-05	1.5E-04	1.6E-04	1.5	4.6	0.4	-1.35	-1.72	0.88	-3.1	0.52
	May.15	0.92	17	-	-	-	1.29	4.43	0.6	-0.58	-1.6	1.63	-1.8	0.84
	Jul.15	0.75	159	9.9E-05	5.6E-04	5.6E-04	0.26	3.39	-0.04	-0.57	-1.47	0.84	-1.8	0.97
Station 2	Nov.14	0.86	31	4.0E-05	2.2E-04	2.1E-04	0.11	1.82	-1.13	-4.41	-2.41	-2.91	-8.7	-1.13
	Feb.15	0.88	20	2.6E-05	1.5E-04	1.4E-04	1.22	4.18	0.03	-1.83	-1.83	0.11	-4.5	0.4
	Mr.15	0.88	26	3.1E-05	1.7E-04	1.6E-04	0.97	3.69	-0.29	-2.42	-1.86	-0.71	-2.2	-0.08
	May.15	0.92	31	3.9E-05	2.3E-04	2.2E-04	1	4.07	0.31	-0.75	-1.56	1.15	-2.4	0.66
	Jul.15	0.73	186	1.5E-04	7.9E-04	7.4E-04	0.66	4.07	-0.25	-1.08	-1.23	0.04	0.9	0.03
Station 3	Nov.14	0.95	24	2.6E-05	1.6E-04	1.4E-04	1.21	4.25	-0.11	-1.84	-1.98	0.1	-4.5	0.49
	Feb.15	0.96	26	2.7E-05	1.8E-04	1.5E-04	1.05	4.01	0.26	-1.09	-1.54	0.77	-3.0	0.63
	Mr.15	0.94	20	2.8E-05	1.8E-04	1.6E-04	0.69	3.53	0.93	0.61	-0.93	2.46	0.2	0.85
	May.15	0.87	29	5.4E-05	2.9E-04	2.4E-04	0.99	3.98	0.18	-1.32	-1.76	0.96	-3.0	0.55
	Jul.15	0.68	440	1.7E-04	9.4E-04	8.7E-04	-0.27	3.09	-0.16	0.45	-1.1	1.44	-0.7	0.94
Station 4	Feb.15	0.90	8	3.8E-05	2.2E-04	1.3E-04	1.34	3.94	0.14	-2.57	-1.91	-0.38	-3.2	-0.03
	Mr.15	0.88	17	2.6E-05	1.5E-04	1.2E-04	0.98	3.8	0.69	-0.6	-1.5	1.56	-1.8	0.87
	May.15	0.60	275	-	-	-	0.49	4.21	0.26	0.42	-0.59	1.3	0.3	0.62

CA: Calcite; DO: Dolomite; GY: Gypsum; BI: Bloedite; EP: Epsomite; GL: Glauberite; PO: Polyhalite; HA: Halite

Table A4 Na/Cl, Mg/Ca, Li/Cl, Br/Cl and B/Cl molar ratios and mineral saturation indices in PW samples of Maharlu Lake (see sampling stations in Fig. 1).

	Date	Depth (cm)	Na/Cl	Mg/Ca	Li/Cl (Molar)	Br/Cl	B/Cl	CA	DO	GY	BL	EP	GL	PO	HA
											Saturation Indices				
Station 1	Nov.14	20	0.89	172	7.6E-05	4.5E-04	4.5E-04	0.45	4.22	0.72	1.94	-0.63	3.15	2.2	1.49
	Feb.15	20	0.87	37	-	-	-	1.23	4.62	0.55	-0.35	-1.12	1.35	-1.2	0.62
	Mr.15	20	0.90	15	3.0E-05	1.7E-04	1.6E-04	1.24	4.19	0.49	-1.11	-1.52	0.96	-2.6	0.55
	May.15	20	0.95	22	-	-	-	1.29	4.55	0.5	-0.51	-1.58	1.57	-1.9	0.83
	Jul.15	20	0.89	233	7.0E-05	3.9E-04	3.7E-04	0.4	3.94	-0.11	0.15	-1.33	1.35	-1.6	2.62
	Nov.14	50	0.92	102	6.4E-05	4.2E-04	2.8E-04	0.43	3.42	0.08	-0.43	-1.13	0.83	-2.0	0.54
	Feb.15	50	0.84	70	-	-	-	0.97	4.43	0.48	0.01	-0.91	1.43	-0.7	2.25
	Mr.15	50	0.86	42	5.1E-05	2.9E-04	2.7E-04	1.02	4.33	0.61	-0.02	-1.04	1.64	-0.8	0.81
	May.15	50	0.97	20	-	-	-	1.4	4.7	0.56	-0.51	-1.58	1.63	-1.7	0.83
	Jul.15	50	0.81	306	8.9E-05	5.0E-04	4.8E-04	0.53	4.28	-0.11	0.1	-1.17	1.15	-1.4	0.92
	Nov.14	100	0.86	112	6.9E-05	4.4E-04	2.6E-04	0.11	2.49	0.34	0.15	-0.9	1.41	-0.7	0.75
	Feb.15	100	0.85	39	-	-	-	1.02	4.28	0.61	-0.12	-1.07	1.58	-0.9	0.75
	Mr.15	100	0.88	38	3.2E-05	1.9E-04	1.7E-04	0.88	3.91	0.28	-0.69	-1.36	0.99	-2.4	0.62
	May.15	100	1.00	29	-	-	-	1.15	4.36	0.33	-0.62	-1.67	1.38	-2.3	0.83
	Jul.15	100	0.86	99	4.2E-05	2.9E-04	1.8E-04	0.38	3.65	0.38	0.65	-1.09	2.09	0.4	1.05
Station 2	Nov.14	20	0.71	269	2.0E-05	8.7E-04	8.5E-04	0.33	3.43	-0.16	-0.57	-1.08	-1.16	-2.3	-0.41
	Feb.15	20	0.83	90	-	-	-	0.72	4.01	0.31	-0.15	-0.89	1.1	-1.3	0.61
	Mr.15	20	0.85	73	2.9E-05	1.4E-03	1.2E-03	0.68	3.58	0.28	-0.28	-1.49	-0.7	-1.5	-0.13
	May.15	20	0.84	64	-	-	-	1.02	4.46	0.35	-0.33	-1.12	1.18	-1.4	0.57
	Jul.15	20	0.70	477	2.2E-05	1.0E-03	9.6E-04	0.33	3.8	-0.01	0.54	-1.11	-0.52	-0.2	-0.02
	Nov.14	50	0.59	192	2.6E-05	1.1E-03	1.1E-03	0.55	3.81	0.62	0.62	-0.65	-0.31	1.2	-0.21
	Feb.15	50	0.61	650	-	-	-	0.1	3.77	0.2	0.83	-0.21	1.24	0.6	0.78
	Mr.15	50	0.62	238	1.9E-05	8.6E-04	8.0E-04	0.53	3.9	0.7	1.18	-0.66	-0.13	2.1	-0.05
	May.15	50	0.69	152	-	-	-	0.75	4.4	0.39	0.24	-0.69	1.34	-0.1	0.61
	Jul.15	50	0.74	394	2.0E-05	9.3E-04	8.5E-04	0.24	3.58	0.15	1.06	-1.03	-0.19	0.6	0.05
	Nov.14	100	0.60	322	2.3E-05	1.1E-03	1.0E-03	0.35	3.63	0.32	0.47	-0.73	-0.6	0.5	-0.21
	Feb.15	100	0.61	623	-	-	-	0	3.63	0.34	1.19	-0.16	1.67	1.4	0.95
	Mr.15	100	0.65	329	2.5E-05	1.1E-03	1.0E-03	0.39	3.74	0.45	0.94	-0.69	-0.36	1.3	-0.09
	May.15	100	0.57	238	-	-	-	0.63	4.42	0.45	0.56	-0.41	1.44	0.9	0.64
	Jul.15	100	0.71	440	1.7E-05	9.5E-04	8.7E-04	0.37	3.83	0.03	0.61	-1.16	-0.52	-0.1	0.02

Abbreviations are similar to Table A3

Table A4 continued

	Date	Depth (cm)	Na/Cl	Mg/Ca	Li/Cl	Br/Cl	B/Cl	Saturation Indices							
					(Molar)			CA	DO	GY	BL	EP	GL	PO	HA
Station 3	Nov.14	20	0.83	65	-	-	-	0.87	4.17	0.51	-0.14	-0.95	1.35	-0.5	0.68
	Feb.15	20	0.65	700	-	-	-	-0.13	3.37	0.24	1.07	-0.13	1.46	1.0	0.86
	Mr.15	20	0.85	75	-	-	-	0.76	3.99	0.3	-0.35	-1.08	1.06	-1.5	0.96
	May.15	20	0.82	55	-	-	-	0.81	4.04	0.54	-0.03	-1.03	1.56	-0.6	0.68
	Jul.15	20	0.69	280	-	-	-	-1.44	0.57	0.28	0.98	-0.76	1.98	0.8	1.03
	Nov.14	50	0.61	208	-	-	-	0.53	4.19	0.68	0.96	-0.26	1.88	1.8	0.83
	Feb.15	50	0.69	699	-	-	-	-0.12	3.39	0.19	1.07	-0.2	1.46	0.9	0.88
	Mr.15	50	0.50	402	-	-	-	0.33	4.01	0.39	0.56	-0.31	1.25	1.1	0.76
	May.15	50	0.60	240	-	-	-	0.46	4.13	0.47	0.74	-0.45	1.66	1.0	0.77
	Jul.15	50	0.62	338	-	-	-	0.09	3.57	0.31	1.06	-0.62	1.95	1.1	0.99
	Nov.14	100	0.57	331	-	-	-	0.12	3.56	0.45	0.79	-0.27	1.51	1.3	0.72
	Feb.15	100	0.63	1066	-	-	-	-0.55	2.66	-0.12	0.96	-0.2	0.81	0.0	0.63
	Mr.15	100	0.70	191	-	-	-	0.19	3.44	0.63	0.9	-0.36	1.87	1.4	0.84
	May.15	100	0.54	426	-	-	-	-0.06	3.36	0.34	0.84	-0.31	1.47	1.1	0.75
	Jul.15	100	0.56	805	-	-	-	-0.73	2.51	0.13	1.34	-0.4	1.81	1.3	1.05
Station 4	Nov.14	20	0.56	196	2.4E-04	1.3E-03	1.2E-03	0.63	4.28	0.54	0.4	-0.28	1.28	1.1	0.48
	Feb.15	20	0.51	443	-	-	-	0.08	3.62	0.59	1.11	0.03	1.68	1.9	0.81
	Mr.15	20	0.49	553	2.2E-04	1.2E-03	1.1E-03	0.05	3.66	0.41	0.94	-0.08	1.42	1.5	0.74
	May.15	20	0.54	266	-	-	-	0.32	3.93	0.46	0.72	-0.42	1.6	1.1	0.72
	Jul.15	20	0.53	1485	2.2E-04	1.1E-03	1.0E-03	-0.79	2.83	-0.08	1.62	-0.34	1.79	1.1	1.1
	Nov.14	50	0.51	441	2.6E-04	1.4E-03	1.0E-03	0.21	3.91	0.52	1.09	0	1.62	1.9	0.69
	Feb.15	50	0.53	557	-	-	-	-0.14	3.34	0.56	1.36	0.02	1.87	2.1	0.95
	Mr.15	50	0.50	223	2.4E-04	1.2E-03	1.1E-03	0.39	3.96	0.83	1.05	-0.09	1.95	2.5	0.81
	May.15	50	0.55	255	-	-	-	0.42	4.08	0.5	0.73	-0.39	1.61	1.1	0.73
	Jul.15	50	0.60	508	1.8E-04	9.9E-04	8.7E-04	-	-	0.26	1.72	-	-	3.0	-
	Nov.14	100	0.71	223	1.5E-04	8.8E-04	4.5E-04	0.26	3.65	0.45	0.8	-0.45	1.7	0.9	0.82
	Feb.15	100	0.53	1764	-	-	-	-0.62	2.82	-0.04	1.07	-0.04	1.07	0.6	0.84
	Mr.15	100	0.48	705	2.2E-04	1.1E-03	9.9E-04	-0.26	3.25	0.48	1.38	-0.05	1.85	2.1	0.99
	May.15	100	0.61	228	-	-	-	0.34	3.85	0.5	0.71	-0.39	1.6	0.8	0.7
	Jul.15	100	0.54	501	1.9E-04	1.0E-03	9.1E-04	-0.67	2.74	0.37	1.85	-0.26	2.39	2.3	1.14

Abbreviations are similar to Table A3

Table A5 The ratios of average major and minor solutes concentrations in SW and PW at station 1 to average values

in input rivers

Parameter	Mg	Ca	SO$_4$	HCO$_3$	Cl	Na	K	Br	TDS
SW/Rivers	86.9	3.4	29.0	0.8	559.2	509.8	51.0	337.8	172.6