Comparative Study of the Major Ion Composition in Eurasian Salt Lakes: Lake Urmia, Lake Issyk-Kul, Aral Sea, and Dead Sea

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Contents

Abstract A comparative study of the major ion composition on the base of the same chemical methods was made for the hypersaline lakes: the Lake Urmia, the Aral Sea,

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the Dead Sea, and the brackish Lake Issyk-Kul. The samples from the investigated lakes with salinity changing from 5 to 328 g kg^{-1} were collected in 2013–2019. Concentrations of anions: chlorides, sulfates, carbonates, and cations: calcium and magnesium were determined with potentiometric titration and potassium with gravimetric method. The density was analyzed with a high-precision method using the density meter Anton Paar DMA 5000M and salinity was also expressed as a total sum of ions. Comparison of the salt compositions of the lakes revealed significant differences in the ratios of their components and their temporal variability due to a changing climate and anthropogenic impact.

Keywords Hydrochemistry, Hypersaline Lake, Modeling, Sediment chemistry, Urmia Lake

Abbreviations

SSW Standard seawater IAPSO (OSIL)
SW Seawater

1 Introduction

The investigated lakes, Lake Urmia, the Aral Sea, the Dead Sea, and Lake Issyk-Kul are located in arid climatic zones. All of them, except for Lake Issyk-Kul, have a significant negative water balance, and their waters are high salty that are classified as brines. They are subject to degradation mainly due to human activities and partly due to natural processes. The water level in them is steadily decreasing. This leads to the precipitation of some ions in the form of salts and the formation of brine. The physical and chemical properties of the lakes also depend on their hydrological features which are discussed in the chapter by Yakushev E. V. et al. [1].

Ionic composition is an important hydrochemical characteristic of natural water. The study of the ion composition of saline water bodies is of particular importance in the use of these waters in certain branches of the national economy, in the mining of mineral resources such as in the Dead Sea (https://www.weizmann.ac.il/sci-tea/Brombook/index.html) [2]. Saline composition plays an important role in the life of hydrobionts. Its change entails changes in the physical properties of the reservoir, the change in biological diversity, and, as a consequence, its complete disappearance such as in the Aral Sea [3]. The study of the chemical composition (hydrochemistry) of lake water is of great practical importance for the development of various sectors of the economy in the region. The chemical composition must be taken into account when using natural waters for all types of water supply and water use. The importance of hydrochemical research is also increasing due to the increase in pollution of water bodies and anthropogenic activities.

Lake Urmia is located at an altitude of 1,275 m. Elongated from north to south; maximum length – about 140 km, width – about 40–55 km. Its average depth is 5.5 m [4], maximum – up to 15 m. Lake Urmia is one of the largest salt lakes on the planet. Its area is about 5,500 km^2 [5]. The lake lately is divided by a causeway into northern and southern basins. Annual fluctuations in the level of the lake range from 20 to 50–60 cm. The hydrological conditions of Lake Urmia are mainly influenced by the climate and topography. Due to the melting of snow in the mountains at the end of spring, the flow of rivers increases, and the water level in the lake rises. The total annual inflow into the lake is 6.900 million m^3 of water, of which 4.900 million m^3 is from rivers, 500,000 m^3 from floods, and 1.500 million m^3 from precipitation [6]. The intake of freshwater drains by the population living in its vicinity has a huge impact on the current state of the lake. Figure 1 shows the state of the Lake in the period from October 2014 to April 2019.

The Aral Sea ceased to exist as a whole and today is a complex of separate water bodies connected by periodically drying channels [3]. Since drying up after 1960 by 2004, the sea has lost 75% of its surface area and about 90% of its water [7]. We report the history of the emergence of individual water bodies of the Aral Sea in our articles [7, 8]. Today, the western basin of the Large Aral Sea is the deepest of the remaining individual bodies of water. Until the 1960s, the Aral Sea level fluctuated at an altitude of about 53.5 m above sea level and had a depth of 66 m. In 2019, according to our calculations, it is about 18 m above sea level. To date, the sea level has dropped by 36 m or 56%. In May 2019, the sea depth was about 30 m. Figure 2 shows schematically the current state of the Aral Sea in comparison with the period before its desiccation according to NASA satellite observations (https://earthobservatory.nasa.gov/world-of-change/AralSea).

These changes were the anthropogenic load on natural sources of freshwater that feeds the lakes, as well as the extraction of minerals in the Dead Sea [9]. Industrial mining for human needs has a huge impact on the chemical composition of the Dead Sea water.

The Dead Sea is more than 400 m below sea level, and its depth today is less than 300 m [10]. The total water deficit in the Dead Sea is 690×10^{-6} m^3 per year. About 36% of this amount comes from the chemical industry in the southern basin [2]. The main reason for the process of obtaining the necessary minerals involves the evaporation of water that flows from the northern basin to the southern one, where the evaporation basins are located. Here halite completely precipitates, and the brine reaches such saturation when carnallite ($KMgCl_3{\cdot}6H_2O$), which is used to produce potash, begins to precipitate. The latter is a target mineral for the production of potash fertilizers. Residual water (about 50% of the volume used) returns to the Dead Sea with a relatively high content of Mg–Ca–Cl with a salinity of 470–500 g l and a density of 1.33–1.35 kg l. This inflow is called the "End Brine" [9, 11]).

The salinity of the Dead Sea today is about 300 g kg^{-1} and more, which is about nine times that of ocean water. In recent years, the sea level has decreased by 1 m per year, mainly due to anthropogenic decrease in the runoff, as a result of industrial extraction of mineral salts [2], as well as general warming on the planet. Figure 3 shows the location of the EG 320 sampling point, where the IOLR and the

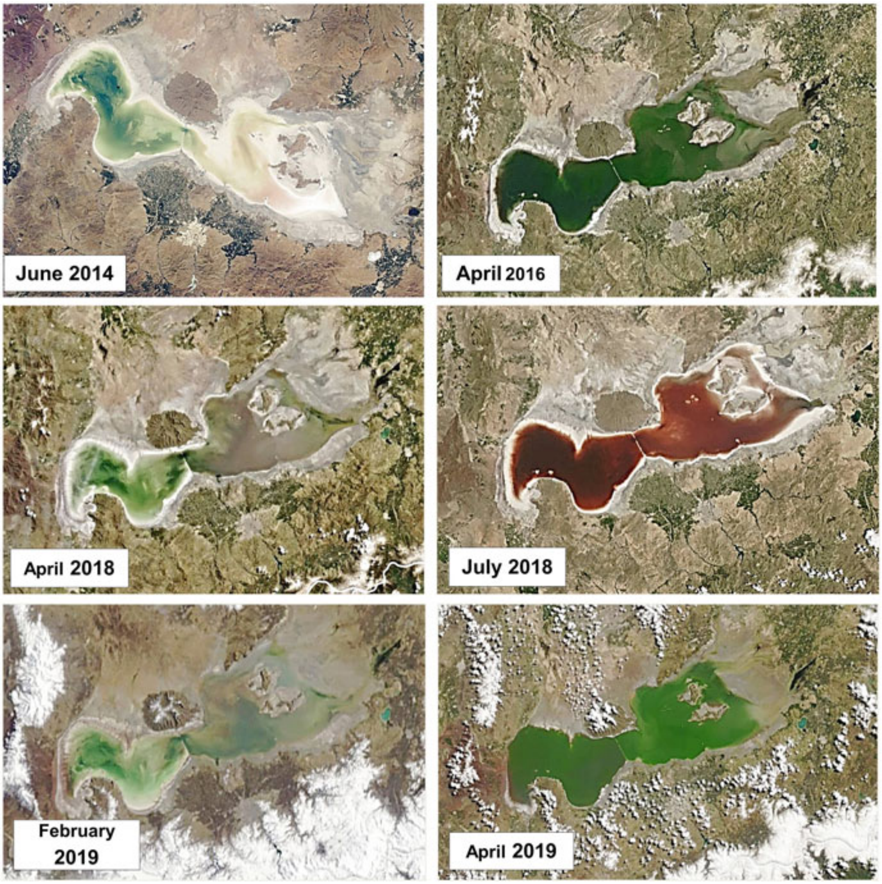

Fig. 1 Current state and fluctuations of Lake Urmia and seasonal variability of its area on NASA satellite images (https://earthobservatory.nasa.gov/images/88395/red-lake-urmia) in the period from October 2014 to April 2019. Dark areas on the lake's surface indicate greater depth, light areas indicate shallowing

Geological Survey (Israel) have been conducting long-term observations of changes in the physical and chemical properties of the Dead Sea water. IO RAS researchers examined samples from this point in May and July 2018 and 2019.

Issyk-Kul Lake is located high in the mountains. It is one of the deepest lakes on the planet with a maximum depth of 668 m [12]. The physicochemical characteristics of Lake Issyk-Kul have not changed significantly over 100 years. Anthropogenic load today does not have a destructive effect on the water resources of the lake. On the contrary, it has decreased over the past few decades. From the work [13] it is known that from 1980 to 2014 there was a decrease in water consumption for irrigation from 2029.42 to 461.76 million m^3 per year, respectively. Water consumption by households during this period decreased from 27.02 million m^3 in 1980

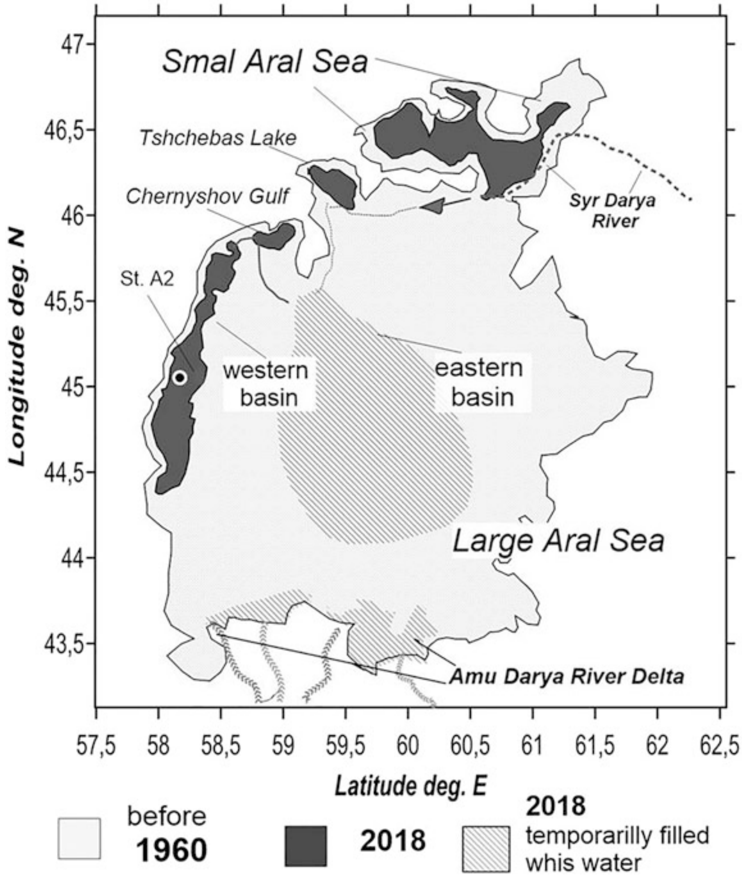

Fig. 2 The modern Aral Sea in 2018 (black aria), before the 1960s (white aria), and temporarily filled with water (dash aria). St. A2 is the sampling area

to 16.55 million m^3 in 2014. The maintenance of the lake water level is favored by the fact that agriculture increases water consumption for irrigation from April to August, but this period is characterized by an increase in atmospheric precipitation. Recent studies have not revealed significant changes in physicochemical characteristics due to climate warming [14], although some researchers note a gradual increase in the salinity of the entire lake over several decades [15]. Data from [14] indicate a positive salinity trend in the inner part of the lake over the past 3 decades, but do not confirm progressive warming of the deep-sea waters of Lake Issyk-Kul, as reported in some previous publications. During the period of our investigation in 2013–2017, the upper layer salinity remained stable. Figure 4 schematically shows a map of Lake Issyk-Kul with a maximum depth of 668 m in the sampling area [14].

This work aims to study (1) the major ionic composition of Lake Urmia, Lake Issyk-Kul, the Aral Sea, and the Dead Sea based on the same technique, (2) the

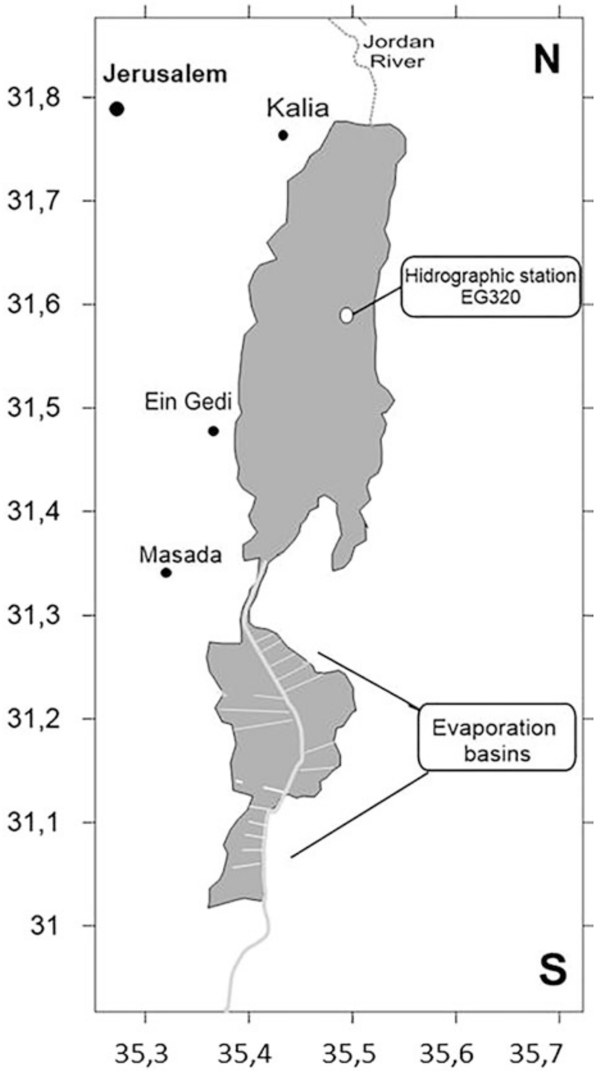

Fig. 3 The modern Dead Sea and its location of the sampling area EG320 on the Dead Sea map

density-salinity ratios of water bodies under study, and (3) the analysis of the resent interannual changes of these lakes with specific emphasis on Lake Urmia.

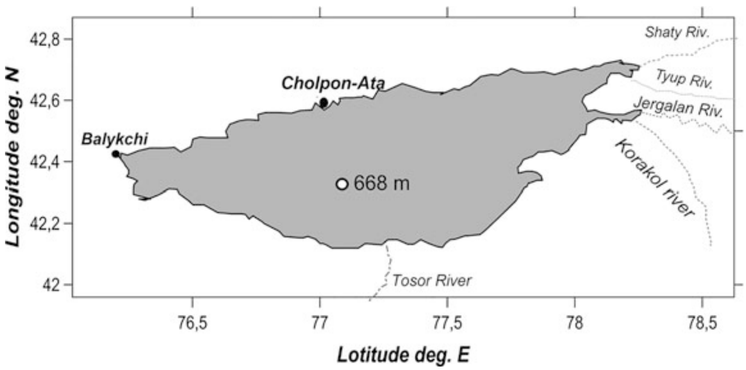

Fig. 4 Map of Lake Issyk-Kull with the sampling area (668 m)

2 Data, Methods, and Equipment

The datasets for this work were received during field expeditions to Lake Urmia, Lake Issyk-Kul, the Aral Sea, and the Dead Sea performed in 2013–2019. Water samples were collected with Niskin bottles or with backets and tranfered into plastic bottles with tight-fitting lids with a volume from 100 to 500 ml. The bottles were filled with a water sample under the lid and hermetically packed and delivered to the laboratory of the IO RAS in Moscow. The collected samples were analyzed in Shirshov Institute of Oceanology, RAS, in Russia and in Iranian National Institute for Oceanography and Atmospheric Science, in Iran. Besides this, we used the published and achieve data for the interannual variability analyses.

Content of major ions in studied lake waters were obtained with standard analytical methods for laboratory determination (for more details, please see [16]), concentration of chlorides, sulfates, calcium, magnesium, total inorganic carbon, and the total alkalinity using potentiometric titration with automatic titrator Metrohm 905 Titrando in g kg^{-1}. For this purpose, the existing methods for the determination of ions were adapted for hypersaline and brackish waters. Indicator electrodes are selected according to the type of reaction and the ion to be determined (Table 1). This complex allows to carry out any potentiometric titration, to measure the pH, the potential, and the temperature of the sample, and to determine the concentrations of anions and cations with high accuracy.

Determination of the concentration of individual ions in saturated brines is associated with certain difficulties. Individual ions can affect the accuracy of the determination of other components. In a potentiometric titration, foreign ions can influence the value of the electrode potential. For example, orthophosphates and iron can interfere with the determination of chlorine ions. During the precipitation of sulfates, calcium coprecipitation is possible [17]. The presence of a large number of ions of iron, copper, cadmium, cobalt, lead, manganese, aluminum, zinc, cobalt, nickel, tin, and increased turbidity can lead to overestimation of the results of determination of calcium and magnesium ions (Russian Gosstandart 31940-2012,

Table 1 Methods of chemical analysis and indicator electrodes

Detected ions	Analysis methods	Electrodes
Cl^-	Precipitation titration titrant, $AgNO_3$ solution	Combination electrode Ag Titrode (Metrohm)
SO_4^{2-}	Precipitation titration titrant, $BaCl_2$ solution	Ba, ion-selective polymembrane (Ecom-Ba) and silver chloride reference electrode
HCO_3^-	Acid–base pH titration with HCl	pH combination electrode iEcotrode plus (Metrohm)
Ca^{2+}	Complexometric titration, EDTA	Combined Ca, selective polymer membrane electrode (Metrohm)
Mg^{2+}		
K^+	Gravimetric determination (precipitation with sodium tetraphenylborate)	
Na^+	Determination of difference between sum of anions and cations in molar equivalent	

2013). The potentiometric titration is high sensitivity and accuracy, ease of use, selectivity, the minimum number of reagents required, as well as the quickness of the analysis.

Potassium ions were measured by a gravimetric method according to [18–20]. The concentration of sodium ions was established by calculating the difference between known amounts of anions and cations [17].

The standard deviations of the methods of the measurement of the major components were no more than: for halogens – 1.7%, for sulfates – 4%, carbonate ions – 1.5%, hydro-carbonate ions – 0.7%, calcium ions – 4%, magnesium – 3.2%, potassium – 1.3% [16].

The required amount of the sample for each analysis was determined experimentally, depending on the salinity of the sample. To prepare reagent solutions and dilute the samples, deionized water (electrical conductivity <0.2 μS s m) was used. The absolute salinity of the samples was determined as the sum of the major ions in g kg^{-1}.

Investigation of the chemical composition is also important for determining the salinity of water since its measurement by the standard hydrophysical equipment on the electrical conductivity is not possible in waters with a non-oceanic ratio of ions [2, 21].

The obtained data were compared with the literature data and the ion composition of the seawater [22].

Field campaign and water analysis in Lake Urmia has been done in four seasons during 2016–2017 by Iran Water and Power Resources Development Company (that outsourced to Asarab Company). Water samples have been taken in shallow Lake Urmia by Van Dorn instrument and in situ water properties including pH, temperature, and conductivity measured by portable Hach multimeter, water turbidity by portable Hach Lange.

High accuracy and precision density measurements of sea and lake water samples were performed using the laboratory density meter Anton Paar DMA 5000 M in the laboratory of SIO RAS and INIOAS. This device applies to any liquid within a wide range of density and viscosity values; the method of measurement does not depend on water ionic composition. The nominal accuracy of density measurements is equal to 10^{-6} g s m^3. Temperature control of a sample with 0.01°C accuracy is provided by two embedded platinum thermometers and Peltier elements. The instrument can automatically vary the temperature of the sample from 0 to 90°C (Operating Instruction, 2010).

The methods for determining the main composition of the lakes were verified on standard samples and standard titers. Each sample was measured in 4–8 replicates. To assess the degree of influence of foreign ions on the result of our measurements, we made an experiment with the samples of SSW with a salinity of 35 g kg^{-1} and samples of water from the Aral Sea with a salinity of about 140 g kg^{-1} [16]. In the course of the experiment, solutions with a known content of the same ions were added to the samples with a known content of the studied ions and titrated. The results obtained were compared with the calculated ones, and the accuracy values were expressed as a percentage. Evaluation of the accuracy of verification measurements of ions showed that the determination of the concentration of ions in the VSP by the methods described above has an error of 1.4–2.8%, and in the water of the Aral Sea sample – 0.6–1.7%.

The major ionic composition of Lake Urmia, the Aral Sea, the Dead Sea, and Lake Issyk-Kul water samples obtained in 2017 was studied in SIO RAS and compared with the SW major ionic composition from [22].

3 Results and Discussions

3.1 Ionic Compositions of the Lake's Samples Obtained in 2017

The studying lakes have many differences in the chemical composition among each other despite the fact that all investigated water bodies are inland drainless lakes and the ion ratios are different from the oceanic ones. For example, the sulfate-chloride mass ratio for Lake Urmia is 0.46, for the Aral Sea is 0.35, for the Dead Sea is 0.003 and for Lake Issyk-Kul is 0.16, and for the SW – 0.14. This suggests that these water bodies belong to different types. Lake Urmia, Lake Issyk-Kul, the Aral Sea, and SW are of sulfate type, and the Dead Sea is of chloride type [23]. The pH of the medium is one of the most important indicators of the chemical composition of seawater, which changes with an increase in the partial pressure of carbon dioxide in the atmosphere. The lowest water pH was found in the Dead Sea water samples. It was 5.85. This indicates a weakly acidic reaction of the Dead Sea water environment. The highest water pH is found in water samples from the Aral Sea and was 8.39 which indicates an alkaline reaction of the environment. The average salinities were: 329 g kg^{-1} for Lake Urmia, 140 g kg^{-1} for the Aral Sea, 284 g kg^{-1} for the Dead Sea, and 6 g kg^{-1} for Lake Issyk-Kul.

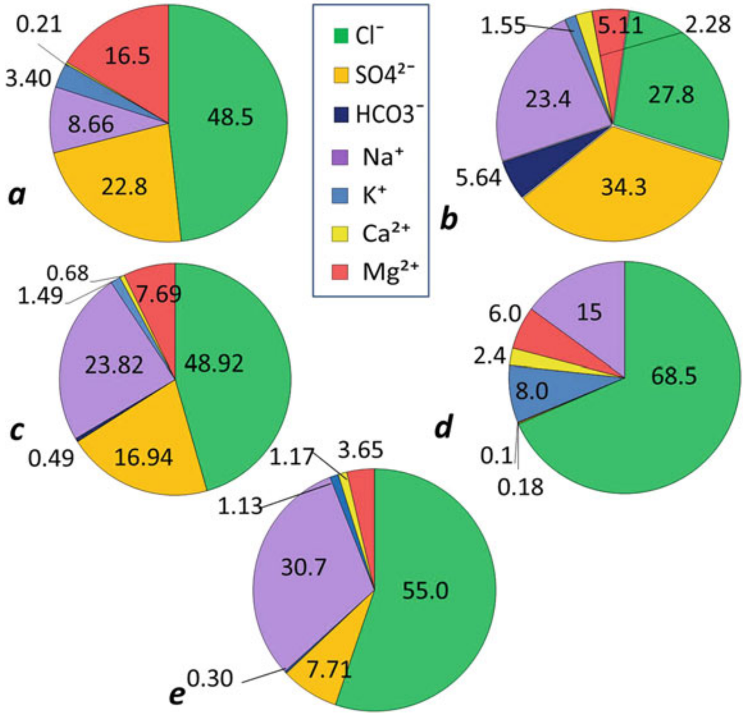

Fig. 5 The content of major ions in upper water samples from: (**a**) Lake Urmia (S = 329 g kg^{-1}); (**b**) Lake Issyk-Kul (S = 5 g kg^{-1}); (**c**) the Aral Sea (S = 140 g kg^{-1}); (**d**) the Dead Sea (S = 290 g kg^{-1}); (**e**) Sea Water (S = 35 g kg^{-1}), in 2017 in percent from total salinity by mass

The total alkalinity of samples was ranged from 2,300 μmol l^{-1} in SSW to 14,250 μmol l^{-1} in the Aral Sea, which depends on the salinity of the sample and increases with increasing the salinity. The total alkalinity A_T is a measure of the ability of an aqueous medium to react with hydrogen ions or the ability of solutes and particles in an aqueous system to neutralize acid (National Field Manual, 2008) and is mainly determined by the content of the dissociation products of carbonic acid, boric acid, and water [17].

Figure 5 shows the relative content of the major components by mass in the upper layer samples in water bodies under study compared with their content in SSW. The content of the main ions in the compositions of these reservoirs differs significantly and affects their physical properties such as density, freezing point, and evaporation rates. From Table 2 it can be seen that in the Aral Sea the proportions of the main ions differ in the surface and bottom layers, because this lake has a two-layer structure.

The obtained concentrations of the main ions are unique information because the composition of enclosed salt lakes is very sensitive to environmental changes. Unlike seawater, the composition of the water of salt lakes is most sensitive to changes in the environment. It changes in conditions such as a decrease or increase

Table 2 Ionic compositions have been analyzed with the following methods

Detected ions	Analysis methods
Cl^-	Gravimetric analysis with ignition of residue, standard method 4,500
SO_4^{2-}	Gravimetric analysis with ignition of residue, standard method 4,500
HCO_3^- CO_3^{-2}	Standard method 2,330
Ca^{2+}	Standard method 3,500 Ca
Mg^{2+}	Standard method 3,500 Mg
K^+	Standard method 3,500 K
Na^+	Standard method 3,500 Na

in the water level in the lake, a change in water temperature, and the influx of minerals with continental runoff waters.

3.2 Density Determination in 2017

Table 3 shows the data on the density and salinity of the Lake Urmia water samples, independently obtained in the laboratories of the two institutes at different times. Salinity values are expressed in g l^{-1}. To assign our salinity value, originally obtained in g kg^{-1} to the general form, we multiply it by the value of the water density of a given sample, which was obtained at the temperature of summer water 32°C. The table shows that the density of water obtained in August is higher than those obtained in January by 3% and the salinity by 37%. It is likely that in summer, water losses in the lake increase as a result of strong evaporation and water withdrawal in the region for household needs by the population.

Table 4 shows that water samples from the lakes differ significantly among themselves both in salinity and in density and from the oceanic water. There is a dependence of density on salinity and, accordingly, on the ion-salt composition inside each basin. The highest density is observed in samples from Urmia Lake and the lowest density in Lake Issyk-Kul. According to the results of this study, it was found that with an increase in temperature for every 2°C, the density values do not decrease equally for the studied lake samples due to different ionic compositions (Table 5). For example, the density value for SSW decreases by an average of 0.06%, for the Aral and Dead Seas and Lake Urmia – by 0.07%, and for Lake Issyk-Kul – by 0.05%.

3.3 The Density and Salinity Ratios

The water density of hypersaline lakes depends on the ionic composition and is very sensitive to any changes in the composition. Therefore, to explain the structure of

Table 3 Concentration of the major components of the ion composition and total alkalinity of water samples of lakes understudy in 2017 and of the SSW

Sample name	Depth, m/location of sampling site	pH	Salinity, g kg^{-1}	Anions g kg^{-1}			Cations g kg^{-1}				AT, μmol l^{-1}
				Cl^-	SO_4^{2-}	HCO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	
Reference seawater [a]	–	8.1	35.165	19.35	2.71	0.11	10.78	0.40	0.41	1.28	2,300
The Aral Sea[b]	0, in-shore	8.26	140.22	68.60	23.75	0.66	33.40	2.09	0.95	10.78	13,946
	0	8.15	140.06	68.517	23.875	0.57	33.24	2.08	0.91	10.87	14,249
	29	8.39	140.62	64.11	28.75	0.62	34.04	1.95	0.94	10.21	13,542
The Dead Sea[b]	0, in-shore	6.23	267.69	182.77	0.63	0.10	22.23	6.38	16.50	39.09	5,198
	0, in-shore	5.85	288.05	197.25	0.52	0.16	22.96	6.913	17.18	43.08	5,146
	0.5, in-shore	6.05	297.37	200.70	0.31	0.16	30.35	6.61	16.23	43.03	5,085
Lake Urmia[b]	0, in-shore	No data	328.87	159.51	74.92	No data	28.47	11.18	0.70	54.09	No data
Lake Issyk-Kul	0	8.3	5.75	1.62	1.99	0.33	1.31	0.07	0.13	0.30	5,658
	50	8.2	5.91	1.63	2.07	0.32	1.45	No data	0.12	0.30	5,519
	350	7.29	5.81	1.61	2.00	0.32	1.37	0.08	0.13	0.230	5,608
	478	7.64	6.06	1.72	2.07	0.33	1.49	No data	0.13	0.32	5,652

[a] Data from [22]
[b] Data from [16]

Table 4 Temperature, density, and salinity of the Lake Urmia

Institute name	Iran water and power resources development									IO RAS
Date	2017-01-16				2017-01-17					2017-08-28
Water temperature (°C)	2.4	2.2	1.4	4.2	2.4	5	5.6	6.3	5.3	32
Density (g ml^{-1})	1.2571	1.2572	1.2571	1.2569	1.2571	1.2378	1.2477	1.2448	1.2398	1.2922
TDS (g l^{-1})	300.2	305.1	317.8	314.9	306.2	276.0	290.8	280.7	278.2	426.1

Table 5 Water samples density of investigated lakes in 2017 and SSW

Sample name	Temperature, °C	21	23	25	27	29
	S g kg^{-1}	Density g s m^3				
SSW	34.996	1.024492	1.023932	1.02334	1.022717	1.022064
Urmia Lake	328.87	1.297146	1.29626	1.295362	1.294467	1.293566
Aral Sea	140.22	1.113940	1.113158	1.112357	1.11154	1.110704
	140.06	1.114072	1.113291	1.112492	1.111673	1.110837
	140.62	1.115151	1.114363	1.113556	1.112732	1.11189
Dead Sea	267.69	1.228858	1.228011	1.227153	1.226289	1.225418
	288.05	1.246148	1.245294	1.244424	1.243546	1.242669
	297.37	1.246823	1.245993	1.245146	1.244296	1.243437
Issyk-Kul Lake	5.75	1.003111	1.002641	1.002131	1.001584	1.001001
	5.91	1.003249	1.002778	1.002268	1.001723	1.001140
	6.06	1.003222	No data	No data	No data	No data

their water, it is important to determine the chemical composition of water as accurately as possible. In Krumgalz and Millero [21], using the example of salts in the composition of the Dead Sea water, estimates of the influence of such factors as temperature, salt composition, and molar volume on water density are given. It was found that the test salts increase the density of the solutions in the order corresponding to the molecular weight of the salt:

$$CaC1_2 > MgC1_2 > KC1 > NaC1$$

In order to describe the interaction of density and ionic composition in the water bodies under study – Aral and Dead Seas and Lakes Issyk-Kul and Urmia, we collected all the available data, both obtained by us and from literature sources where density data were available. Based on the collected materials, we have compiled plots that reflect the ion–density interaction in the waters of the studied lakes.

The density presented on plots is expressed by the density anomaly, which is calculated by the formula:

$$\Delta\rho = (\rho - \rho_0) \times 1{,}000$$

where $\Delta\rho$ is the density anomaly in kg m^3, ρ is the density of the sample in g sm^3, ρ_0 is the density of distilled water in g sm^3, and 1,000 is the conversion factor in kg m^3.

Figures 6, 7, 8, and 10 show the impact of salt compositions on the water density for the lakes understudy. The plots were compiled based on observational and historical data. As an example of the density-salinity relations in the Aral Sea, the graph was built based on the data of the surface layer of the deep-water part of the western basin of the Large Aral Sea. Graph 10 for Lake Issyk-Kul was straightforward based on depth data, as no temporal variability in the composition of the lake water was found.

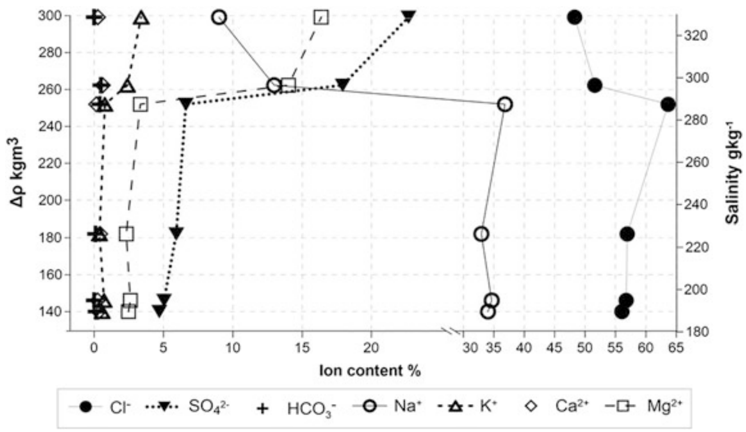

Fig. 6 The dependence of the density on the salt composition of Lake Urmia water according to the results of observations during 1987–2019

Lake Urmia. Figure 6 shows a graph compiled from studies of the density and ionic composition of Lake Urmia from 1987 to 2017. To compile the Urmia Lake database, the following literary sources were used: [24] for 1987 data, [25] for 1991 data, [26] for 2002 data, [4] for 2008 data, data of the Iran Water and Power Resources Development for 2016 data and [16] for 2017 data. During the period from 1987 to 2017, salinity increased 1.8 times, and density doubled, which caused a significant metamorphization of the ionic composition.

Due to its shallow depth, the composition and properties of the Lake's water are extremely subject to seasonal variability. The selection of freshwater continental runoff and groundwater for the needs of the population living in the region significantly affects the level of Urmia. In turn, the drying up of the Lake causes changes in its physical and chemical properties. Studies show that chlorides and sodium predominate in the composition of water, and with an increase in the concentration of brine, the content of sulfates and magnesium significantly increases. Consequently, intense precipitation of halite occurs, and such conservative ions as potassium and magnesium remain in the solution. Additionally, the ionic composition alters due to significant intra-annual fluctuations in the lake level.

Aral Sea. The relationship between the density and ionic composition of the Aral Sea, as well as its change over time, is shown in Fig. 6 for the example of the deep-water part of the western basin of the Large Aral Sea. To compile the Aral Sea database, the following literary sources were used [3] for 2007 data [16], for 2014–2017data [8], for 2018–2019 data.

The maximum depth in this part of the lake is about 30 m, and the water column has a two-layer structure ([3, 27]. At present, the salinity value is about 140 g kg^{-1}. It increases every year and has seasonal fluctuations along with fluctuations in the level of the lake. It was found that with an increase in salinity on average for every 1 g kg^{-1} both in the surface and bottom layers, the density increases on average by

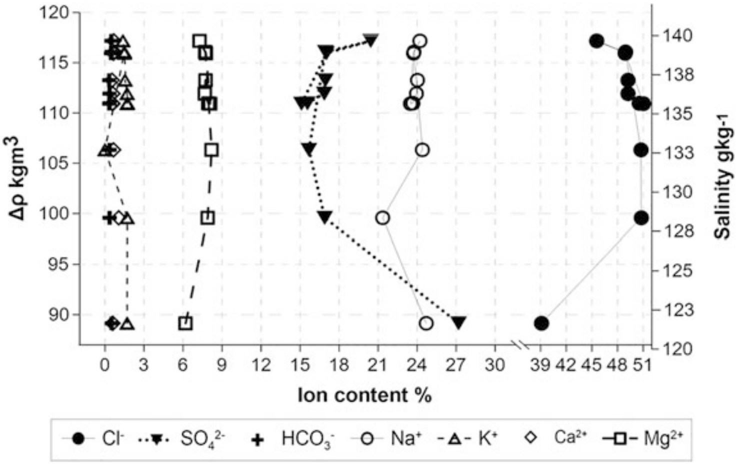

Fig. 7 The dependence of the density on the salt composition of the Large Aral Sea water according to the results of observations during 2007–2019

1.2 kg m^3, but these changes do not occur linearly. They depend on the ionic composition of water [8]. The change in salinity both in time and depth is accompanied by a change in the ratio of the main ions and density. Figure 7 shows that at the level of 140 g $kg^{-1}$and 138 g kg^{-1}on the salinity scale, the content of sulfate ions is increased, and the content of chlorides is decreased in comparison with the previous salinity values. These values correspond to the bottom layers of the lake in 2017 and 2019. They have a composition and density different from the surface and intermediate layers, that is, both thermohaline and density stratification are observed here. In general, the graph shows that a decrease in chlorides and an increase of sulfates in the content in time contribute to the Aral Sea water density.

Investigation of the relationship between ionic composition and density in individual water bodies of the Aral Sea showed that separate parts of the lake in the process of drying up and dividing acquired their physicochemical properties. The reason for these differences lies in the different hydrological regimes of these reservoirs. Depth, area, and distance from the continental runoff led to forming different ionic compositions. According to these properties, separated basins began to differ not only from each other but also within the same reservoir, e.g., the Large Aral and the Chernyshev Gulf. As a result, density, evaporation, and freezing temperatures in each water body are now different [3, 8, 27].

Dead Sea. Figure 8 shows the change in density as a result of a decrease in sea level and an increase in salt concentration from 2002 to 2019. To compile the Dead Sea database, the following literary sources were used: 2002 data from [9], 2005–2013 data from [10], 2017 data from [16], 2018–2019 our data. According to our observations, during this period, the salinity of the lake increased by 10%, and the density – by 7%. The density of water in 2019 was 1.246 g cm^3. The changes in the ratio of the main ions in the Dead Sea water caused by seasonal fluctuations in the

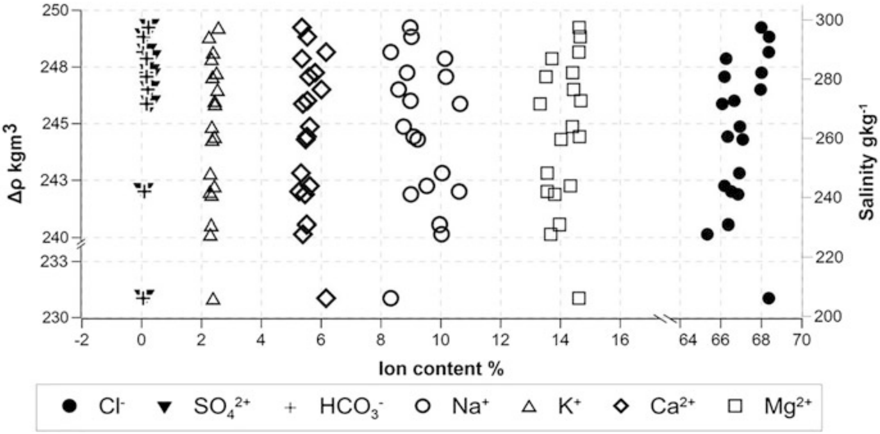

Fig. 8 The dependence of the density on the salt composition of the Dead Sea water according to the results of observations during 2002–2019

salinity of the lake increase or decrease, but not linearly. So, for the year of our observations from July 2018 to July 2019, the relative content of halogen ions in the composition of the upper layer of the Dead Sea water was more than in previous years by an average of 0.5%, and magnesium cations – by 9%. Changes in the concentrations of other ions remained within the determination error.

An example of the relationship between density and salinity according to IOLR data in the Dead Sea water column is shown in Fig. 9. The red circles and red lines on the graph show the temperature structure, and the blue circles and blue lines show the density structure over depth from 0 to 282 m in 2019 point EG 320.

The density and salinity of water in the surface layer are in some cases higher than in the intermediate and bottom layers, which is associated with evaporation and a higher temperature of the surface layer. This phenomenon usually occurs earlier in the summer and fall. In the middle of summer, at a depth of 100 m in winter, water is formed with complete convective mixing. In the upper layer, from May to September, salinity increases due to evaporation, and the lower layer is transformed in summer under the influence of advection of brines from evaporator pools (return wastewater) and is described in detail in [2, 9, 10]. The figure shows the surface, intermediate, and bottom layers. The density and temperature in the lower layer are slightly higher than in the intermediate layer – this is an indicator of the inflow of more saline and denser End Brine waters. Water temperature data obtained by IOLR personnel during sampling confirms the influence of End Brine. The observed temperature in the lower layer was about 1°C above the intermediate temperature.

Issyk-Kul Lake. The salinity fields in Issyk-Kul are surprisingly conservative. Its interannual changes are measured only in hundredths of a ppm. This situation is possible only if the entire water column is mixed on seasonal and interannual scales intensively. Therefore, the interannual runoff variability can be leveled by the latter mixing in a much larger volume of lake waters [12]. Figure 10 shows a plot of the

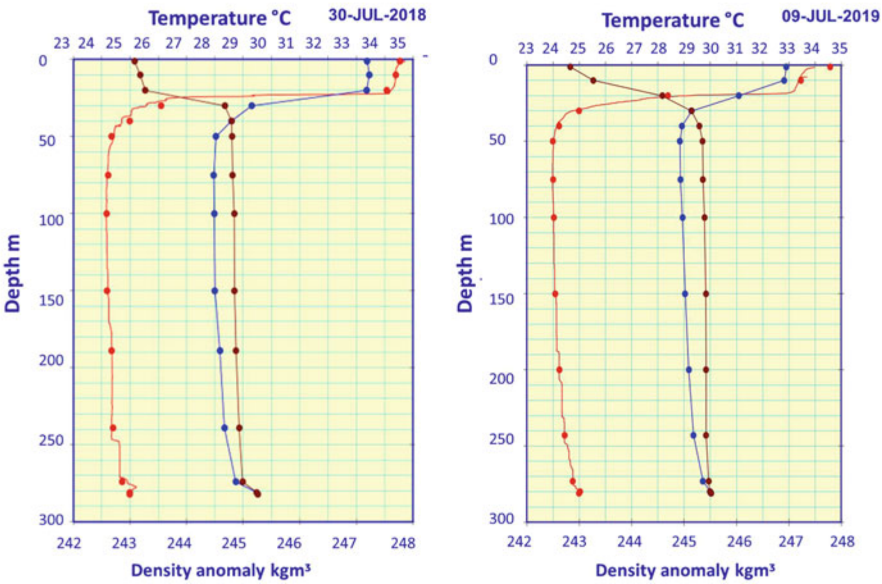

Fig. 9 The red circles on the graph indicate the temperature distribution over depth from 0 to 282 m in 2018, 2019. Distribution of temperature (red circles and red line) and density (blue circles and blue line) at depths from 0 to 282 m in 2019 in the deepest part of the Dead Sea (station EG 320). The plots are taken from https://isramar.ocean.org.il/isramar2009/DeadSea/Default.aspx

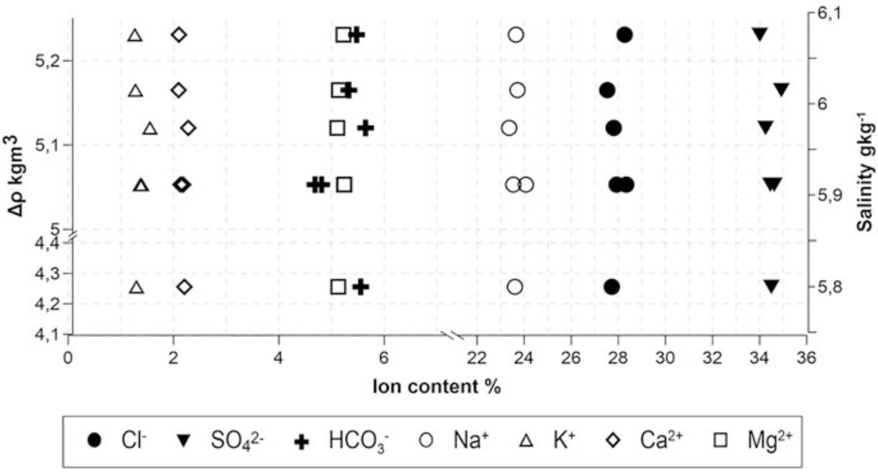

Fig. 10 The dependence of the density on the salt composition of Lake Issyk-Kul waters according to the results of the observations during 1987–2017

relationship between density and ionic composition in the waters of Issyk-Kul Lake from 2013 to 2017. To compile the Issyk-Kul Lake database, the following literary sources were used: data of IO RAS research (2013–2019). The figure shows that the increase in density in the lake is influenced by the increase in salinity with depth. Changes in salinity and significant changes in ionic composition in the lake are not observed. It is noticeable that, despite the great depth, the content of the main ions in the water composition has only small fluctuations, which do not exceed Cl^- – 2.8%, $SO_4{}^{2-}$ – 1.9%, $HCO_3{}^-$ 2%, Na^+ – 2.4%, K^+ – 7.8%, Ca^{2+} – 2.3%, Mg^{2+} – 2.9% of the average.

Our data do not support the reports of progressive warming of the deep waters of Issyk-Kul. However, they indicate a positive salinity trend in the inner part of the lake over the past 3 decades, which agrees with the results of Zavialov et al. [14].

4 Conclusion

In this work, we studied major ionic composition, density-salinity ratios, and their interannual changes in Lake Urmia, Issyk-Kul Lake, the Aral Sea, and the Dead Sea. These studies were carried out using techniques adopted for the measurements in the high salinity conditions. The comparison of the main salt compositions of the studied water bodies showed significant differences among the lakes. It also revealed that the salt compositions of the lakes are different than the seawater ones, which indicates the non-sea origin of these waters. It was confirmed that Lake Urmia, Issyk-Kul Lake, the Aral Sea are of sulfate type, while the Dead Sea is of chloride type. There also can be marked clear differences in pH (changing from 5.85 in the Dead Sea to 8.39 in the Aral Sea) and total alkalinity (changing from 5,085 μmol l^{-1} in the Dead Sea to 14,250 μmol l^{-1} in the Aral Sea). The highest density was found for the samples from Urmia Lake and the lowest density in Issyk-Kul Lake. It was found that due to different ionic compositions the density does not vary equally with the changes in the thermal field of these lakes.

It was also shown that, unlike seawater, the composition of the water of salt lakes is most sensitive to changes in the environment due to the water level fluctuation, changes in water temperature, and the influx of minerals with continental runoff waters. Our results indicate that occurred changes in the salt composition of Lake Urmia and the Aral Sea over the past decades are irreversible due to the absence of continental runoff. The compositions of the Dead Sea and Issyk-Kul Lake are almost constant over the last decades. However, the salinity and density of the Dead Sea increased steadily, and Issyk-Kul Lake was more susceptible to seasonal fluctuations.

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References

1. Yakushev EV, Andrulionis NY, Jafari M, Lahijani HAK, Nooran P (2021) How climate change and human interaction alter chemical regime in salt lakes, cases study: Lake Urmia, Issyk-Kull Lake, Aral Sea and Dead Sea. Chapter of the book Peygham G. Nooran, Evgeniy V. Yakushev, Ole Anders Nøst, Jorn Bruggeman. 2020. In: Lake Urmia: a hypersaline waterbody in a drying climate. Hdb. Env. Chem. Springer
2. Gertman I (2012) Dead Sea L, Bengtsson RW, Herschy RWF (eds) Encyclopedia of lakes and reservoirs. https://doi.org/10.1007/978-1-4020-4410-6
3. Zavialov PO (ed) (2012) The large aral sea in the beginning of century 21: physics, biology, chemistry. Nauka, Moscow. 229 p. (in Russian)
4. Karbassi A, Bidhendi GN, Pejman A, Bidhendi ME (2010) Environmental impacts of desalination on the ecology of Lake Urmia. J Great Lakes Res 36(3):419–424. https://doi.org/10.1016/j.jglr.2010.06.004
5. Fazeli Nashli H, Wong EH, Potts DT (2005) The Qazvin plain revisited. Anc Near East Stud 42:3–82. https://doi.org/10.2143/ANES.42.0.2004448
6. Ghaheri M, Baghal-Vayjooee MH, Naziri J (1999) Lake Urmia Iran: a summary review. Int J Salt Lake Res 8(1):19–22. https://doi.org/10.1007/BF02442134
7. Zavialov PO (2005) Physical oceanography of the dying Aral Sea. Chichester, Springer/Praxis. 146 p
8. Andrulionis NY, Zavialov PO, A.S., I. (2021) Modern evolution of the salt composition of the Aral Sea. Oceanology 61(6):925–935. https://doi.org/10.1134/S0001437021060035
9. Final Report (2011) Dead Sea Study. Red Sea to Dead Sea Water Conveyance (RSDSC) Study: Dead Sea Research Team, 2011Red Sea – Dead Sea Water Conveyance Study Program GSI Report Number: GSI/10/2011, TAHAL Report Number: IL-201280-R11-218, Team Leader: Elias E1, Editor: Esakov S1 et al., pp 31–36
10. Stiller M, Lensky N, Gavrieli I (2018) Recent evolution of the dead sea chemical composition: 2005-2015. Technical report book, Jerusalem, https://doi.org/10.13140/RG.2.2.15272.62722
11. Lensky NG, Dvorkin Y, Lyakhovsky V, Gertman I, Gavrieli I (2005) Water salt and energy balances of the Dead Sea. Water Resour Res 41(12). https://doi.org/10.1029/2005WR004084
12. Zavialov PO, Izhitskiy AS, Kirillin GB, Rezvov VY, Alymkulov SA, Zhumaliev KM, Kurbaniyazov AK (2020) Features of thermohaline structure and circulation in Lake Issyk-Kul. Oceanology 60(3) (in Russian)
13. Alymkulova B, Abuduwaili J, Issanova G, Nahayo L (2016) Consideration of water uses for its sustainable management the case of Issyk-Kul Lake Kyrgyzstan. Water 8(7):298. https://doi.org/10.3390/w8070298
14. Zavialov PO, Izhitskiy AS, Kirillin GB, Khan VM, Konovalov BV, Makkaveev PN, Pelevin VV, Rimskiy-Korsakov NA, Alymkulov SA, Zhumaliev KM (2018) New profiling and mooring records help to assess variability of Lake Issyk-Kul and reveal unknown features of its thermohaline structure. Hydrol Earth Syst Sci 22:6279–6295. https://doi.org/10.5194/hess-22-6279-2018
15. Kawabata Y, Kurita T, Nagali M, Aparin V, Onwona-Agyeman S, Yamada M, Fujii Y, Katayama Y (2014) Water quality in the Lake Issyk-Kul and the river flowing into it. J Arid Land Stud 24-1:105–108

16. Andrulionis NY, Zavialov PO (2019) Laboratory studies of main component composition of Hyperhaline Lakes. Phys Oceanogr 26(1):13–31. https://doi.org/10.22449/1573-160X-2019-1-13-31
17. Millero FJ (2013) Chemical oceanography. CRC Press, Boca Raton, 591 p. http://b-ok.xyz/ireader/2571941
18. Culkin F, Cox RA (1966) Sodium, potassium, magnesium, calcium and strontium in seawater. Deep-Sea Res 13:789–804
19. Kremling K (2007) Determination of the major constituents. In: Grasshoff K, Kremling K, Ehrhardt M (eds) Methods of seawater analysis. WILEY-VCH. Chapter 11, Weinheim, pp 229–251. https://doi.org/10.1002/9783527613984.ch11
20. State Standart 23268.7-78 (n.d.). Mineral drinking medicinal water, medical table and natural table. Methods for the determination of potassium ions. IPK Izdatel'stvo standartov, Moscow, 4 p. (in Russian)
21. Krumgalz BS, Millero FJ (1982) Physico-chemical study of Dead Sea waters: II. Density measurements and equation of state of Dead Sea waters at 1 atm. Mar Chem 11(5):477–492
22. Millero FJ, Feistel R, Wright DG, McDougalld TJ (2008) The composition of standard seawater and the definition of the reference-composition salinity scale. Deep Sea Res Part 1 Oceanogr Res Pap 55(1):50–72. https://doi.org/10.1016/j.dsr.2007.10.001
23. Valyashko MG (1962) Regularities of the formation of deposits of potassium salts. Publishing House of Moscow University, Moscow. 398 p. (in Russian).
24. Touloie J (1998) Hydrogeochemistry of Urmia Lake. The first oceanology conference of Iran, Tehran, pp 20–23.
25. Emamali-Sabzi R (1993) Separation of some salts from Urmia Lake by crystallization. MSc thesis. Tarbiat Moddares University, Iran
26. Alipour S (2006) Hydrogeochemistry of seasonal variation of Urmia Salt Lake, Iran. Saline Syst 2(Article no. 9), 19 p. https://doi.org/10.1186/1746-1448-2-9
27. Izhitskiy AS, Zavialov PO, Sapozhnikov PV, Kirillin GB, Grossart HP, Kalinina OY, Zalota AK, Goncharenko IV, Kurbaniyazov AK (2016) Present state of the Aral Sea: diverging physical and biological characteristics of the residual basins. Sci Rep 6:c. 23906