

Effect of Variations in the Ion-Salt Water Composition on the Accuracy of Salinity Measurements

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Abstract

Purpose. The work is aimed at assessing the effect of variations in the major ion-salt composition on the accuracy of determining water salinity in the inland seas and other seawater areas. The main goal of the study is to assess the representativeness of the results of the CTD salinity measurements (standard in oceanological practice) for the areas where the ion-salt seawater composition differs from that of the ocean.

Methods and Results. Salinity values of the seawater samples collected in the expeditions in the Black Sea and the Kerch Strait, and also in the Kara and Caspian seas in 2014–2021, were obtained in four different ways: 1) measurements with a CTD-probe based on electrical conductivity (practical salinity); 2) based on the measured density values, calculation by the TEOS-10 equation of state with due regard for the regional correction for the areas under study (absolute salinity); 3) calculation by chlorine content using empirical dependencies for the corresponding water basins; 4) direct calculation based on a sum of components of the major ionic composition (similar to chemical determination in a laboratory).

Conclusions. Differences in the ratios of the main ions in the water chemical compositions of the water areas and basins under study significantly affect the accuracy of salinity determination by standard oceanographic equipment. The variations in the major ionic composition, especially in the surface layer of the sea coastal part, are assumed to be largely influenced by the continental freshwater runoff. The ionic composition variability, having been not taken into account, leads to the errors in the measurements of physical parameters at traditional CTD-probing.

Keywords: determination of salinity, salinity, ionic composition, chemical composition, component composition, density of seawater, seawater, potentiometric titration, Black Sea, Kerch Strait, Caspian Sea, Kara Sea

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1. Introduction

Attempts to determine the seawater salinity have been undertaken since ancient times and have acquired more or less quantitative forms from the 17th century¹. Salinity is defined as the mass of minerals dissolved in 1 kg of seawater. However, there are many such substances, so it is difficult in practice to measure

¹ Zolotov, Yu.A., ed., 2002. [*Fundamentals of Analytical Chemistry. In 2 Volumes. Volume 1. General Questions. Separation Methods: Textbook for High Schools*]. Moscow: Vyschaya Shkola, 351 p. (in Russian).



accurately their total content in each seawater sample [1]. By the beginning of the 19th century, it became known that the relative content of the major salt components of seawater in the ocean is constant with a fairly high (but, as it turned out later, not absolute) accuracy (the principle of constant proportions, or Dietmar's law), so it is enough to determine the content of any one element in order to calculate total salinity. The most convenient parameter for measurement was the concentration of chlorides, or chlorinity [2]. Chlorinity was measured using direct titration and then converted to salinity using a simple linear function ². At present, an improved ratio for oceanic water [3] is used, and its regional variants, for example, for the waters of the Caspian [4, 5] and Black seas [6], are also applied.

Since the early 1980s, salinity measurements are mainly carried out with CTD- (conductivity, temperature, depth) probes and are based on electrical conductivity, more precisely, on the ratio of the electrical conductivity of seawater to the conductivity of a special reference sample ³ (IAPSO Standard Seawater), which is taken from the surface in a certain area of the Atlantic Ocean [2]. The values of the seawater electrical conductivity at a fixed ion-salt composition are completely determined by salinity, temperature and pressure. The density dependence on temperature, salinity and pressure is determined by EOS-80 equation of state.

In 2010, a new international thermodynamic equation for seawater state TEOS-10 [7] was adopted. It relates the seawater density to its temperature, absolute salinity, and pressure. This equation, at a known density, can be applied to determine salinity very accurately, requiring special densiometric equipment to measure density independently.

The most reliable salinity values can be obtained from direct laboratory chemical concentrations of the major seawater ionic components [8] as the sum of the major ions. For some saline water bodies, such as, for example, the Aral Sea ⁴ [9–12], the Caspian Sea [13], and other water areas, this method is essentially the only one possible for the correct determination of salinity values. However, the salinity determination by the sum of the major ions is a rather laborious process, which also requires laboratory conditions and equipment.

Based on both field CTD-probing and laboratory studies of the ion-salt composition and density of samples taken during expeditions, the authors of the proposed work set themselves the task to analyze quantitatively the deviations from each other in salinity values obtained by all of the abovementioned methods. The main goal of the study was to assess the representativeness of the results of CTD salinity measurements, standard in oceanological practice, for the areas in which the ionic-salt composition of seawater differs from the “canonical” oceanic one. When writing the article, the materials of the dissertation were used ⁵.

² Alekin, O.A. and Lyakhin, Yu.I., 1984. *Chemistry of the Ocean*. Leningrad: Gidrometeoizdat, 343 p. (in Russian).

³ OSIL, 2020. *IAPSO Standard Seawater*. [online] Available at: <https://osil.com/salinity-measurement-standards/> [Accessed: 09 September 2022].

⁴ Blinov, L.K., 1956. [*Hydrochemistry of the Aral Sea*]. Leningrad: Gidrometeoizdat, 232 p. (in Russian).

⁵ Andrulionis, N.Yu., 2022. [*Ion-Salt Composition of Waters of Marine Areas and Inland Water Bodies and Its Influence on Their Hydrophysical Characteristics*]. Thesis Cand. Geogr. Sci. Moscow, 140 p. (in Russian).

2. Materials and methods

Water samples from the Black Sea surface were obtained during coastal expeditions in 2014–2021 (Fig. 1, Table 1).

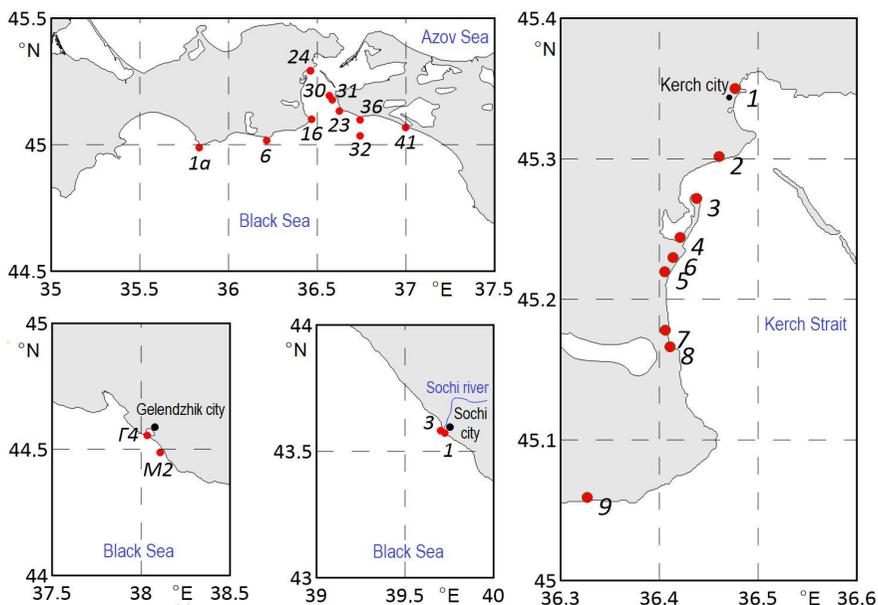


Fig. 1. Location of sampling stations in the Black Sea (2014–2021)

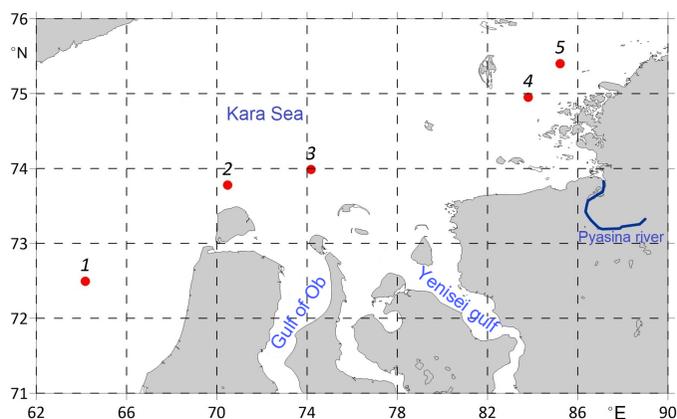


Fig. 2. Location of sampling stations in the Kara Sea (2018)

Water samples from the Kara Sea were obtained during the expedition of R/V *Akademik Mstislav Keldysh* (cruise No. 73) in 2018. The samples were taken from the surface in five areas of the sea: westwards of the Yamal Peninsula at a distance of about 160 km from the coast, near Belyi Island – about 60 km off the coast, near Shokalsky Island – about 120 km off the coast, as well as between the Taimyr Peninsula (60 km off the coast) and the Arcticheskiy Institut Islands (70 km off the coast) (Fig. 2).

Table 1

Location coordinates, names of the stations and water sampling dates

Location of sampling	Date of sampling	Station number	Station coordinates	
			° N	° E
Kara Sea	September 25–26, 2018	1	72.494444	64.170000
		2	73.776667	70.476111
		3	73.984722	74.174167
		4	74.951111	83.805556
		5	75.401111	85.222220
Black Sea, from the Feodosiya Bay to the Kerch Strait	May 1, 2019	1a	44.987528	35.835806
		6	45.012694	36.209528
		24	45.291056	36.461444
		31	45.183333	36.592972
Kerch Strait	September 1–8, 2019	12	45.071708	36.461732
		17	45.103928	36.482090
		20	45.119100	36.555908
		23	45.135783	36.623403
		24	45.288658	36.457697
		28	45.223365	36.535535
		31	45.182142	36.589330
	July 1, 2020	6	45.016460	36.215190
		16	45.100560	36.468800
		23	45.132810	36.623840
		24	45.291690	36.460600
		30	45.193770	36.567890
		31	45.178270	36.583490
		32	45.034790	36.740890
	December 15–16, 2021	36	45.099130	36.741730
		41	45.066560	36.998340
		1	45.349800	36.476900
		2	45.301800	36.460700
		3	45.271700	36.437500
		4	45.244200	36.421200
		5	45.219800	36.405700
		6	45.229700	36.413600
		7	45.178100	36.405900
Black Sea, river Sochi estuary	May 27, 2014	8	45.166400	36.410700
		9	45.059200	36.327143
Black Sea, river Sochi estuary	May 27, 2014	1	43.573000	39.722000
		3	43.583000	39.699000
Black Sea, the Gelendzhik Bay	October 1, 2020	M2	44.498883	38.125930
		Γ4	44.569766	38.033283
Caspian Sea, river Ural estuary	April 11–12, 2016, April 14–17, 2017	9	46.874490	51.344090
		12	46.784050	51.577190
		17	46.741570	51.525490

Water samples from the Caspian Sea surface in the area near the mouth of the Ural (Zhaiyk) River were obtained during coastal expeditions in 2016 and 2017 (Fig. 3).

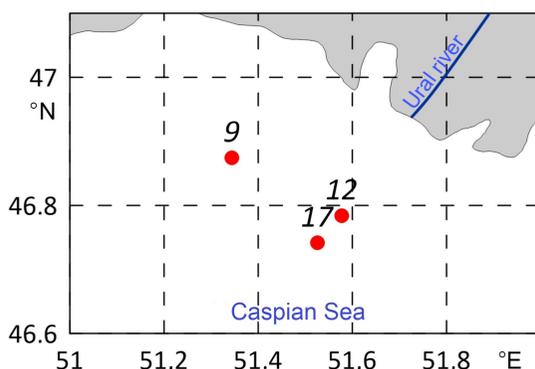


Fig. 3. Location of water sampling stations in the Caspian Sea (2016 and 2017)

The water samples were placed in plastic bottles of 1 or 1.5 l in volume, which were pre-rinsed with water from the sample taken, sealed and delivered to the laboratory for further analysis. After determining the total alkalinity and total dissolved inorganic carbon according to the method described in the sources⁶ [14], the samples were filtered through a GF/F Whatman 0.7 μm membrane filter to remove mineral and organic suspension and placed in glass containers of 100–250 ml in volume. To prepare reagent solutions and dilute samples, we used deionized water (conductivity < 0.2 $\mu\text{S}/\text{cm}$), which was obtained using a laboratory deionizer. The reaction of the solution medium during the analysis was monitored using a Metrohm combined pH electrode. The mass of the analyzed sample was measured by weighing on an OHAUS laboratory analytical balance of the first accuracy class with 0.001 g error.

Measurements of the water density of the studied samples were carried out using Anton Paar DMA 5000M precision density meter. The error in measuring the water density⁷ was $\pm 10^{-5}$ g/cm^3 . The density of the samples was measured at temperatures from 1 to 29 °C at atmospheric pressure. Before starting the work, the measuring cell was washed with ethyl alcohol at a concentration of 95% and deionized water. For each sample, 3–4 measurements were performed. The mean value was taken as the result. The maximum root-mean-square deviations of sample density amounted to 0.3 kg/m^3 for the Black Sea, 0.2 kg/m^3 for the Kara Sea, and 0.02 kg/m^3 for the Caspian Sea.

Salinity values were determined in several ways. Practical salinity (*SP*) was measured simultaneously with sampling during the expeditions using CastAway (SonTek, USA), Rinko (JFE Advantech, Japan), and SBE 19plus (Sea-Bird, USA)

⁶ Guidance Document RD 52.10.743-2010 “*Total Alkalinity of Sea Water. Measurement Technique by Titrimetric Method*”. Moscow, 20 p. (in Russian); Guidance Document RD 52.10.243-92. “*Guide to Chemical Analysis of Sea Waters*”. Saint Petersburg, 264 p. (in Russian).

⁷ Anton Paar GmbH, 2012. *Instruction Manual DMA 4100 M, DMA 4500 M, DMA 5000 M*. Austria: Anton Paar GmbH, 152 p.

CTD-probes. The salinity calculation using TEOS-10 equation based on density measurements with an Anton Paar DMA 5000M density meter was performed using the MATLAB software with GSW Oceanographic Toolbox⁸ package installed, which is recommended by TEOS-10 developers. To determine the seawater salinity using chlorinity values, the equations developed both for ocean water [8] and for the waters of the Black [6], Kara [3], and Caspian [4, 5] seas were used. The value of chlorinity was obtained by the classical titration method (Mohr method), namely, precipitation of halogens with silver nitrate⁹ [2]. To determine the salinity of waters as the sum of the major ions (hereinafter, *SS*), the obtained concentrations of the major composition components were summarized. To determine the concentrations of components of the major ionic composition of the water bodies under study, a Metrohm 905 Titrando (Switzerland) automatic potentiometric titrator, equipped with indicator electrodes, was applied. The apparatus characteristics and the methodological features of its application are described in more detail in our paper [10].

In order to control the accuracy of measurements, similar determinations of the concentrations of major ions and density were also carried out on IAPSO standard seawater samples with a total practical salinity of 34.993 PSU, specially designed for calibrating instruments and verifying salinity measurements. The maximum deviation between the determination of salinity by the sum of ions and the absolute salinity of seawater from [3] was 0.08 g/kg.

The concentration of sodium ions was determined as a difference between the sum of anions and cations in mol equivalents. This method provides good results if all other ions are determined with sufficiently high accuracy¹⁰ [8]. To verify the accuracy of this method in the laboratory of the Testing Center of Moscow State University, control determinations of the sodium ions concentration were performed by atomic emission spectroscopy in accordance with GOST R 57165-2016. The maximum difference between the average calculated value of sodium ions concentration and the averaged measurement data was 0.2 g/kg for a water sample from the Kerch Strait.

The SSW density was determined in the temperature range from 1 to 29 °C and the obtained values were compared with those calculated using TEOS-10 and EOS-80 formulas in order to evaluate the discrepancy in determining the density in two ways and, consequently, the accuracy of the apparatus (Fig. 4). The deviations of the SSW density values calculated using EOS-80 from the values obtained using a density meter averaged 0.2%, and when calculated using TEOS-10, an average of 0.003% from the values given by the density meter was obtained. This once again indicates the preference for using the new TEOS-10 equation of state for hydrophysical studies in the sea water. The density (σ_T , kg/m³) in Fig. 4 is determined by the formula $\sigma_T = \rho \cdot 1000 - 1000$, where ρ is water density, g/cm³.

⁸ Pawlowicz, R. and McDougall, T.J., 2010. *Thermodynamic Equation of Seawater*. [online] Available at: <https://www.teos-10.org/software.htm> [Accessed: 08 September 2022].

⁹ Morachevsky, Yu.V. and Petrova, E.M., eds., 1965. [*Methods for the Analysis of Brines and Salts*]. Moscow; Leningrad: Chemistry, 399 p. (in Russian).

¹⁰ Reznikov, A.A., Mulikovskaya, E.P. and Sokolov, I.Yu., 1970. [*Methods of Analysis of Natural Waters*]. Moscow: Nedra, 488 p. (in Russian).

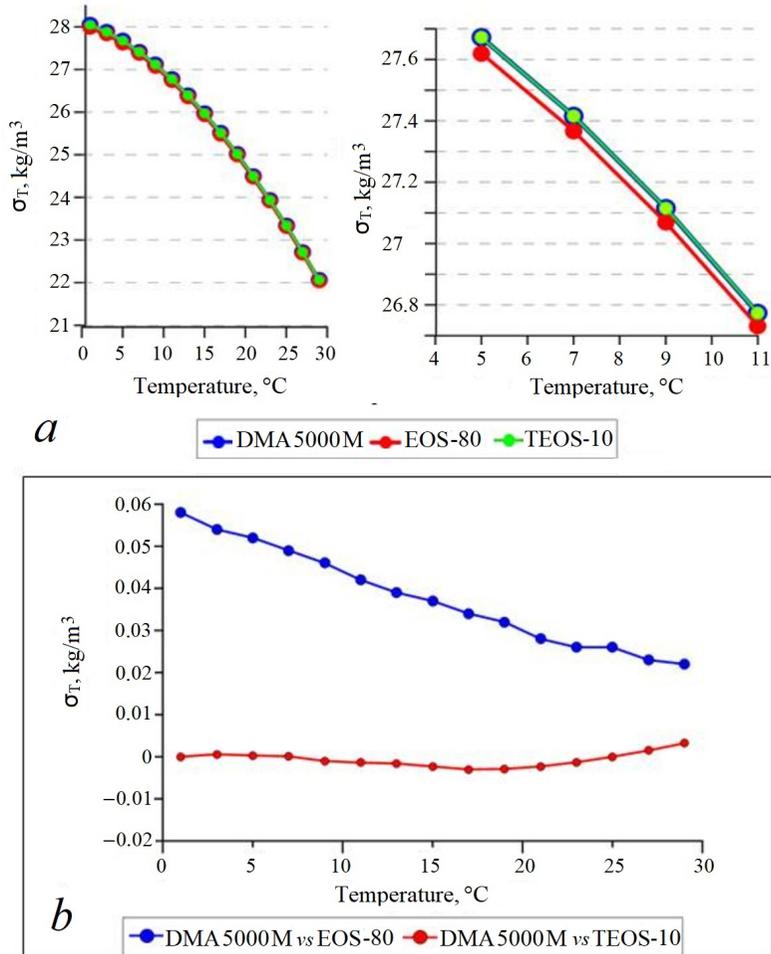


Fig. 4. SSW density obtained in three ways: direct measurement using a density meter (DMA 5000M), calculation by salinity determined from electrical conductivity using EOS-80, and calculation by salinity using TEOS-10 (a); deviations of the SSW density values calculated by EOS-80 and TEOS-10, from those obtained using a density meter (DMA 5000M) (b)

3. Results

3.1. The Kara Sea

The nature of the salinity spatial distributions in the Kara Sea in connection with the propagation of desalinated plumes of the Ob, Yenisei, and other rivers was discussed in many works (for example, [15–18]). The salinity of the studied water samples of the Kara Sea ranged from 14 to 31 g/kg. The deviations of salinity values obtained from the electrical conductivity during CTD-probing from the values received as the sum of the major ions (ΔS), from the chlorinity (ΔS_{Cl}), and from TEOS-10 equation based on direct laboratory measurements of density (ΔST) are given in Table 2.

Table 2

Deviations of the salinity values obtained by electrical conductivity during CTD-soundings, from the values resulted as a sum of the major ions (ΔS), by chlorine content (ΔS_{Cl}) and by the *TEOS-10* equation based on direct laboratory density (ΔST) measurements for the water samples from the Kara Sea

Parameter	Station				
	1	2	3	4	5
ΔS	3.0	1.4	2.2	0.0	0.8
ΔS_{Cl}	2.4	1.2	1.4	1.7	0.2
ΔST	1.0	0.6	0.2	1.5	1.1

Note: the ΔS , ΔS_{Cl} and ΔST values are presented as a percentage of the sample total salinity (by weight).

From Table 2 it can be seen that the deviations of the salinity values obtained from the electrical conductivity from the values obtained by other methods are from 0 to 3.0% for the studied samples.

The ratios of the major ions in the studied water samples of the Kara Sea differed from the “canonical” oceanic ionic composition, i.e. similar ratios for the SSW (Fig. 5).

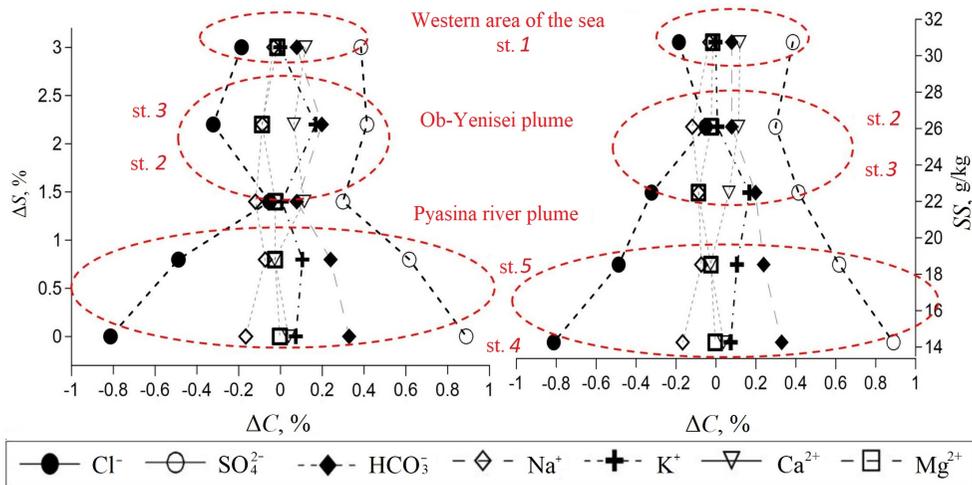


Fig. 5. Deviations (in percent by weight) of the content of major composition components in the studied samples from their content in SSW, and the relationship of these deviations with salinity and ΔS , as well as with the location of a sampling station

A correlation between these deviations and the location of the sampling station is also observed. It is clearly seen that, firstly, deviations of the composition from 470

the oceanic (ΔC) are most clearly manifested in the waters of low salinity, desalinated by continental runoff, and, secondly, these deviations are expressed primarily in an increased content of sulfate ions and a reduced content of chlorine ions.

According to our data, the content of SO_4^{2-} ions (as well as the hydrocarbonate ion HCO_3^-) in all samples from the Kara Sea was higher than in the SSW. In the samples from stations 1–3 and 5, the ratio $\text{SO}_4^{2-}/\text{Cl}^-$ (equal to 0.14 for SSW) was more than 0.15, and at station 4 – more than 0.16, that is, the differences from the SSW composition in this indicator exceeded 13%.

As for the relative concentrations of other major ions, their deviations from the SSW composition were less significant, although they were also determinable. Thus, Ca^{2+} content in samples from stations 3–5 turned out to be 0.1–0.2% higher than in SSW, and in samples from stations 1 and 2, it approximately corresponded to the content in the SSW. K^+ content in the samples from stations 1–3 was higher by 0.1% than in the SSW, and at stations 4 and 5 it corresponded to SSW. Na^+ content in all samples was lower on average by 0.1% than in SSW, and Mg^{2+} content almost did not differ from its content in SSW.

Thus, the studies have demonstrated that salinity measurements using CTD-probing in the Kara Sea can lead to errors of up to 3% (several tenths of PSU). The features of the major ionic-salt composition of the Kara Sea are expressed primarily in the content of sulfate ions, an increased concentration of which (in relation to chloride ions) is observed in the areas affected by continental runoff. On the geochemical barrier river – sea, exchange processes occur. They lead to the transformations of the dissolved elements' runoff in the sorbed complex of freshwater terrigenous material, which are described in detail in [19]. It is known from this work that when terrigenous substances penetrate into the marine environment, ion-exchange transformation of the runoff of the dissolved substances occurs. The results of experimental data revealed that the actual Ca^{2+} input into the ocean with river runoff increases by 8.3–8.7% in the process of desorption of ions from solids, while the input of Na^+ , K^+ и Mg^{2+} , on the contrary, decreases by 14.0–14.6; 22.2–23.3 and 3.0–3.2% of their removal in the composition of river water runoff. The estimates demonstrated that the dissolution of 1 meq Ca^{2+} from terrigenous material is accompanied by absorption of about 0.72, 0.13, and 0.15 meq Na^+ , K^+ and Mg^{2+} from seawater. The ion exchange processes also affect the increase in the content of dissolved forms of microelements in the runoff, such as Mn^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Tl^+ , Ba^{2+} and NH_4^+ , and the decrease in the content of Pb^{2+} , Cs^+ .

3.2. The Black Sea and the Kerch Strait

Since the proportion of freshwater runoff in the Black Sea water balance is much larger than in the ocean as a whole, the average salinity on the Black Sea surface (17.85 PSU) is almost half as much as the salinity of the World Ocean surface waters. The practical salinity, averaged over the entire volume of the Black Sea, is 21.96 PSU, in 0–300 m layer – 20.26 PSU, in the layer deeper than 2000 m – 22.26 PSU [18]. The deviations of the Black Sea water salinity values, determined by various methods, from the salinity values determined using the CTD-probe, are presented in Table 3.

Table 3

Deviations of the salinity values obtained by electrical conductivity during CTD-soundings from the values resulted as a sum of the main ions (ΔS), by chlorine content (ΔS_{Cl}) and by the TEOS-10 equation based on direct laboratory density measurements (ΔS_T) for the water samples from the Black Sea and the Kerch Strait

Parameter	Station number																Mean value	RMS deviation										
	1a	2	3	4	5	6	7	8	9	12	16	17	20	23	24	28			30	31	32	36	41	MZ	Γ4			
<i>1. Kerch Strait, May, 2019</i>																												
ΔS	3.02	-	-	-	-	3.02	-	-	-	3.05	-	-	-	-	3.02	-	-	2.69	-	-	-	-	-	-	2.98	0.20		
ΔS_{Cl}	0.17	-	-	-	-	0.17	-	-	-	0.84	-	-	-	-	0.17	-	-	0.20	-	-	-	-	-	-	0.20	0.22		
ΔS_T	1.12	-	-	-	-	1.12	-	-	-	1.14	-	-	-	-	1.12	-	-	1.55	-	-	-	-	-	-	1.48	0.70		
<i>2. Kerch Strait, September, 2019</i>																												
ΔS	-	-	-	-	-	-	-	-	-	-	2.48	3.23	3.46	3.09	3.25	-	-	3.84	-	-	-	-	-	-	-	3.20	0.38	
ΔS_{Cl}	-	-	-	-	-	-	-	-	-	-	1.27	2.21	1.64	2.12	1.03	-	-	2.09	-	-	-	-	-	-	-	1.60	0.52	
ΔS_T	-	-	-	-	-	-	-	-	-	-	1.29	1.52	1.35	1.53	1.76	-	-	1.48	-	-	-	-	-	-	-	1.44	0.18	
<i>3. Kerch Strait, July, 2020</i>																												
ΔS	-	-	-	-	-	2.85	-	-	-	-	2.87	-	-	2.39	1.94	-	2.70	1.97	2.88	2.12	2.22	-	-	-	2.44	0.37		
ΔS_{Cl}	-	-	-	-	-	0.67	-	-	-	0.41	-	-	0.47	0.39	-	0.40	-0.69	0.65	0.25	0.33	-	-	-	-	0.32	0.38		
ΔS_T	-	-	-	-	-	1.48	-	-	-	1.14	-	-	1.70	1.20	-	1.60	1.50	2.37	1.09	1.27	-	-	-	-	1.48	0.37		
<i>4. Kerch Strait, December, 2021</i>																												
ΔS	2.10	-	2.70	2.20	2.30	2.50	2.40	2.60	2.40	2.47	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.47	0.18	
ΔS_{Cl}	0.80	-	-0.33	0.98	0.43	1.30	0.68	0.58	0.41	-0.01	0.54	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.54	0.47	
ΔS_T	1.61	-	3.26	1.67	2.31	1.70	2.07	2.41	2.48	1.90	2.16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.16	0.50	
<i>5. Estuary of river Sochi, May, 2014</i>																												
ΔS	2.49	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.50	1.01	
ΔS_{Cl}	1.39	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.41	0.02	
ΔS_T	3.13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.18	0.95	
<i>Gelendzhik Bay, September, 2020</i>																												
ΔS	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.57	3.00	0.29
ΔS_{Cl}	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.31	3.11	0.10
ΔS_T	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.69	1.40	0.14

Note: the ΔS , ΔS_{Cl} and ΔS_T values are presented as a percentage of the sample total salinity (by weight).

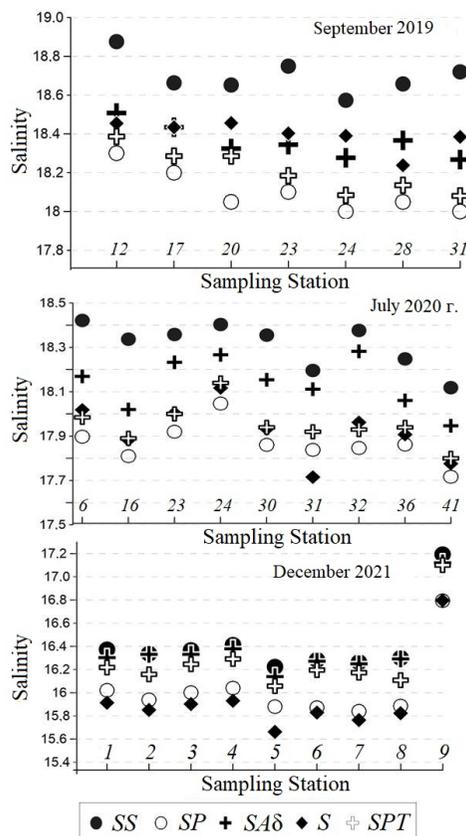


Fig. 6. Salinity values of the water samples from the Kerch Strait (2019–2020) obtained in different ways: summing of principal ions (*SS*), recalculating the electrical conductivity (*SP*), using the TEOS-10 equation (*SA* is the absolute salinity which takes into account the regional correction (*SA δ*) to *SP*, and *SPT* is the practical salinity of a sample calculated by density [7]) and by chlorine content using the ratio (*S*) from [6]

The salinity values of water samples from the Kerch Strait, obtained by various methods in 2019–2020, are presented in Fig. 6.

Similar studies were carried out for water samples taken near the mouth of the Sochi River in May 2014, during the passage from the Feodosiya Bay to the Kerch Strait in May 2019, and also from the Gelendzhik Bay in October 2020.

The highest deviations in all areas were noted for ΔS , i.e. the difference between the CTD-probing data and the sum of ions (up to 3.5% or 0.6 g/kg, near the mouth of the Sochi River during the spring flood). The smallest ΔS values (2.44% or 0.5 g/kg) correspond to the July measurements in the Kerch Strait. The salinity calculations by chlorinity and by TEOS-10 equation based on density measurements provide somewhat better agreement with CTD measurements, however, they also show significant discrepancies (up to 2% or more). In general, the determination of *SA δ* using TEOS-10 equation gave the results that are the closest to *SS*, which is especially evident in the samples from the Kerch Strait.

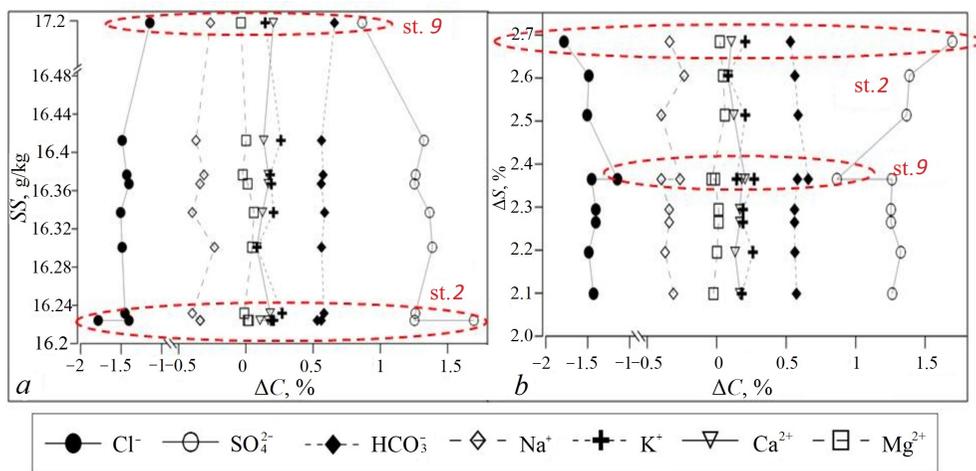


Fig. 7. Deviations in the content of major ions in the compositions of the studied water samples taken in the Kerch Strait (December, 2021) from their content in SSW, and the relationship of these deviations with SS (a) and ΔS (b)

Fig. 7 shows the graphs of the content of the major composition components in the samples of the Kerch Strait waters of different salinity, taken in December 2021, and the related deviations ΔS . It can be seen that the maximum deviations of the ionic-salt composition from the oceanic one were noted at station 2, the waters in its area were the most desalinated among all stations by the Sea of Azov waters. At the same station, the errors of CTD measurements of salinity ΔS were also the greatest (with regard to salinity values calculated from the sum of salts), reaching 2.7% here. On the contrary, in the water at station 9 characterized by the highest salinity and, consequently, the smallest proportion of freshwater runoff, the differences in the ionic composition from the SSW composition were the smallest. As for the analyzed samples of the Kara Sea, the differences in the ion-salt composition from the ocean in the areas of continental runoff effect are also manifested in the Kerch Strait, primarily in an increase in the sulfate-chloride ratio, and also (to a lesser extent) in a reduced Na^+ content and an increased K^+ and HCO_3^- content. The processes of the dissolved elements runoff transformation under the effect of exchange processes in the sorbed complex of freshwater terrigenous material at the geochemical river – sea barrier are described in [19].

3.3. The Caspian Sea

The Caspian Sea is an inland water body not connected with the World Ocean; therefore, the ratios of the major ions in its waters are very different from their ratios in the SSW. In addition, the ionic composition of the sea waters is not the same in different areas due to the strong effect of river runoff [13]. In this regard, the correct salinity measurement in the Caspian Sea presents significant difficulties.

Fig. 8 demonstrates the deviations of the major components of the ion-salt composition of the Caspian Sea water at the mouth of the Ural (Zhayyk) River on the SSW composition along with the corresponding salinity values calculated as

the sum of ions, and in Fig. 9 – salinity values of water samples from the estuarine seashore area of the Ural River of the Caspian Sea, obtained by various methods, including those calculated using previously published special regional formulas for determining the salinity of the Caspian Sea waters by chlorinity (S) [4] and density by chlorinity (S_p) [5]. The latter formula has the following form:

$$(\rho - \rho_0) / S = 0.924 \pm 0.00015,$$

where ρ is the density of the Caspian Sea water sample; ρ_0 is distilled water density.

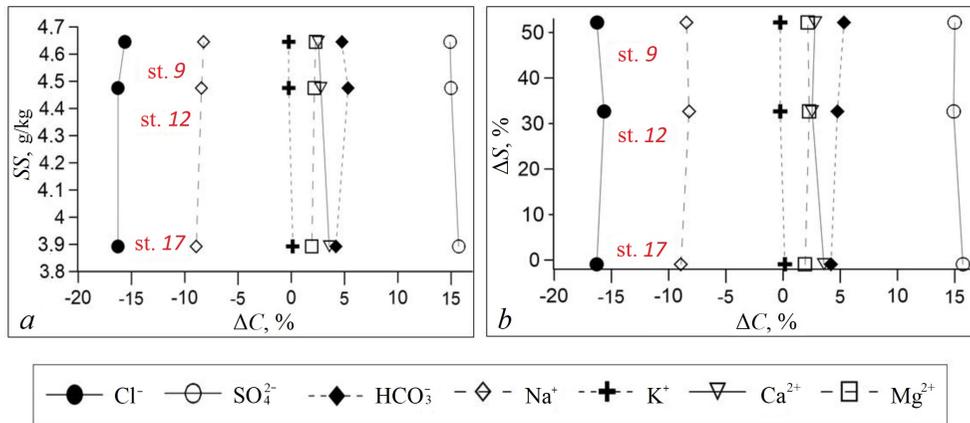


Fig. 8. Deviations in the content of major ions in the composition of the studied water samples taken in the Caspian Sea with different salinity from their content in SSW in 2016, and the relationship of these deviations with SS (a) and ΔS (b)

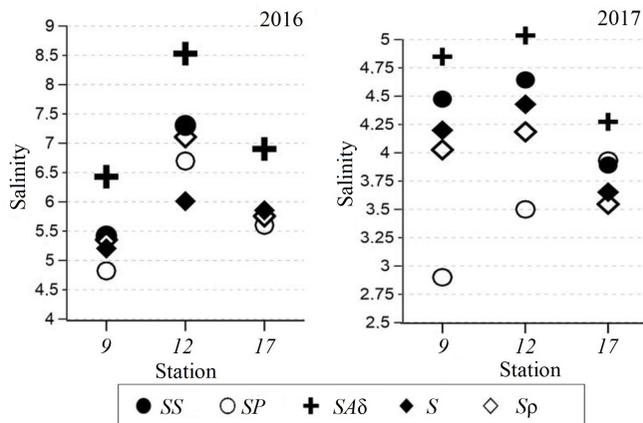


Fig. 9. Salinity of the water samples from the estuary region of the river Ural in the Caspian Sea (2016–2017) obtained by different methods

It should be noted that the relative content of chloride ions in the studied samples of the Caspian Sea waters is on average 15% lower, and sulfate ions content – by the same amount higher than in the SSW. The significant chemical features of these waters should also include a 4% lower content of Na⁺ (relative to SSW) and an increased content of other cations. The content of calcium ions exceeded their content in SSW by an average of 2%.

The results of the major salt composition study also indicated its significant interannual variability. Thus, the content of sodium ions in the samples of 2016 was lower than in the SSW by 3%, and in the samples of 2017 – by 8%. The content of potassium ions was lower than in SSW, on average by 0.2% in 2016 and by 0.1% in 2017. And the content of magnesium ions, on the contrary, was higher than in the SSW by 0.1% in 2016 and 2% in 2017.

In [4], a deviation of about 1.4 g/kg (13%) was reported in the salinity values calculated from the electrical conductivity from the values calculated from the density in the southern part of the Caspian Sea with a total water salinity of 10–12 g/kg. Similar deviations in the Caspian Sea northern part for the estuary seashore of the Ural River amounted to 0.2–1.1 g/kg (3–27%) (Fig. 9). In Table 4, the deviations of the salinity values obtained from the electrical conductivity from the values received by other methods for the waters of the studied samples are given.

As can be seen from Table 4 and Fig. 9, for the waters of the Caspian Sea, the values of practical salinity determined by standard CTD-probing in almost all cases turn out to be strongly underestimated in relation to the results of independent determinations by other methods. If the sum of salts is taken as the “reference” value, then this underestimation reaches 1.6 g/kg, or 52% (!), with a practical salinity of the sample of about 2.9 PSU.

Table 4

Deviations of the salinity values obtained by electrical conductivity during CTD-soundings from the values resulted as a sum of the major salt components ions (ΔS), by chlorine content (ΔS_{Cl}) and by the TEOS-10 equation based on direct laboratory density measurements (ΔST) and by density by means of the regional ratio (ΔSp) [5] for the water samples from the Caspian Sea

Parameter	Station number			Mean value	RMS deviation
	9	12	17		
<i>April, 2016</i>					
ΔS	12.20	9.10	3.60	8.33	2.05
ΔS_{Cl}	7.30	11.40	4.30	7.67	1.68
ΔST	24.91	21.48	18.78	21.7	1.45
ΔSp	9.85	5.81	2.61	6.09	1.71
<i>May, 2017</i>					
ΔS	52.20	32.70	-1.00	27.97	12.69
ΔS_{Cl}	30.00	20.90	-7.70	31.36	13.49
ΔST	64.93	43.91	8.73	39.19	13.39
ΔSp	26.95	16.33	-10.78	25.26	12.39

Note: the ΔS , ΔS_{Cl} and ΔST values are presented as a percentage of the sample total salinity (by weight).

4. Discussions

In the ion-salt composition of the seawater of all the considered water areas, there are clearly recorded differences from the oceanic composition. They are expressed primarily in a shift in the sulfate-chloride ratio towards its increase, i.e. in an increase in the relative content of sulfate ions (by 0.4–0.8% for the Kara Sea, 1.0–1.8% for the Black Sea and the Kerch Strait, 14–16% for the Caspian Sea) and a similar decrease in the relative content of chloride ions. In these areas, there is also a decrease in the relative content of sodium ions (0.1–0.2% for the Kara Sea, 0.1–0.5% for the Black Sea and the Kerch Strait, 1–5% for the Caspian Sea) due to an increase in the content of other cations, as well as bicarbonate ions. These deviations are inversely related to salinity, i.e. they become more pronounced, the larger the proportion in the sample belongs to freshwater continental runoff.

The deviations of the ion-salt composition from the SSW composition lead to the fact that salinity values according to the results of CTD-probing are systematically underestimated. For the studied samples, this underestimation reached up to 3% (or about 1 g/kg) in the Kara Sea, up to 3.5% (or about 0.6 g/kg) in the Black Sea, and up to 52% (or about 1.6 g/kg) in the Caspian Sea. For the Black and Caspian seas, the errors in salinity values according to CTD data are generally greater, the greater the deviation of the ionic composition (expressed, for example, in the sulfate-chloride ratio) from the SSW composition, as expected. However, for the samples from the Kara Sea, such a regularity could not be found. Thus, the performed studies show that the errors in salinity determinations associated with variations in the ion-salt composition in water areas affected by continental runoff are significant and must be taken into account in oceanological practice.

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Petr O. Zavialov – participated in setting the goals and objectives, field research and sampling, development of approaches to the analysis of laboratory material, writing and editing the text of the paper

Aleksandr S. Izhitskiy – participated in field studies and sampling, as well as in the preparation of the graphic material of the paper

The authors have read and approved the final manuscript.

The authors declare that they have no conflict of interest.