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Original article

Major Ionic Composition of Coastal Waters of the Northeastern Black Sea

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Abstract
Purpose. The purpose of the work is to study the variability of major ionic composition and salinity in the coastal zone the northeastern Black Sea over the period 2022–2025, to analyze its causes, as well as to assess the impact of major ionic composition on the accuracy of salinity determination by the classical (chlorinity) and modern (TEOS-10) methods.

Methods and Results. The water samples were collected in the coastal water area from the city of Anapa to the Lazarevskoye settlement (Sochi) during the expeditions in September 2022, in June, September and December, 2023, in August 2024, and in March and August, 2025. The concentrations of major ions ($Cl^-, SO_4^{2-}, HCO_3^-, Ca^{2+}, Mg^{2+}$) were determined by the potentiometric titration method, K^+ gravimetrically, and Na^+ by calculation method. The water salinity values were calculated in three ways: by the sum of major ions, by chlorinity, and by density using the TEOS-10 thermodynamic equation. Density was measured by a high-precision laboratory densitometer. Salinity of the studied water samples varied from 8.77 to 19.11 g/kg (average is ~ 18.40 g/kg). The relative content of Cl^- varied within the range 52.6–54.6%, SO_4^{2-} – 7.8–12.9%, HCO_3^- – 0.8–1.4%, Na^+ – 29.9–31.5%, Ca^{2+} – 1.1–1.8%, and Mg^{2+} – 3–3.7%. The highest deviations of major ionic composition from the oceanic one correspond mainly to the low salinity waters, and this fact indicates the decisive role of freshwater continental runoff in the modification of major ionic composition. The deviation of chlorinity-based salinity calculation from the one based on sum of ions were up to 5% (~ 0.9 g/kg) in the coastal sea waters with salinity 19 g/kg, and 11% (~ 0.9 g/kg) directly in the river mouth waters with salinity 9 g/kg, and the deviation of density-based salinity calculation using the TEOS-10 equation constituted 4% (0.7 g/kg) in the coastal sea waters with salinity 19 g/kg. A correlation between the increase in $SS - S_{Cl}$ difference and the increase in SO_4^{2-}, HCO_3^- и Ca^{2+} contents in water composition was established; when assessing the $SS - SA_\rho$ difference, no such correlation was observed.

Conclusions. A comparison of three methods for determining salinity – by the sum of ions (SS), by the chlorine coefficient (S_{Cl}), and using the SA_ρ density values – has shown that the most accurate values are obtained by the ion sum method. This method makes it possible to define the causes of salinity change due to seasonal variations in the concentrations of certain ions (SO_4^{2-}, HCO_3^-, and Ca^{2+}) in the coastal waters. A comparative analysis of the results revealed a trend towards increasing salinity in the coastal waters of the Black Sea northeastern shelf over the observation period 2022–2025.

Keywords: northeastern shelf of the Black Sea, Krasnodar Krai, ion composition, seawater salinity, seawater density, Black Sea

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Introduction

The major ionic composition (MIC) of the Black Sea waters is formed by the same components as those of all seas and oceans on Earth, namely Cl^-, SO_4^{2-}, HCO_3^-, Na^+, K^+, Ca^{2+} and Mg^{2+}. However, the Black Sea waters are characterized by differences in the relative content (mass fraction) of some components from their content in oceanic water [1]. The reference oceanic water is IAPSO Standard Seawater (SSW), designed for instrument calibration and verification of salinity measurements [2]. MIC anomalies relative to this water composition lead to errors in determining physical parameters by methods developed for oceanic water [1, 3, 4].

MIC anomalies in the Black Sea waters result from the specific features of their formation. The Black Sea, on the one hand, is an inland sea of the Atlantic Ocean basin, and on the other hand, the world's largest meromictic water body with a depth of up to 2212 m [5]. Its hydrographic regime is characterized by low-salinity surface waters mixed with river runoff and more saline deep waters inflowing from the Mediterranean Sea. From a depth of ~150–170 m, the sea is filled with anoxic waters containing hydrogen sulfide, which account for almost 80% of the total water volume [6]. The practical salinity of surface waters in the central Black Sea is usually 17.85–18.40 PSU (practical salinity units), and on the northwestern shelf 14–16 PSU (although higher values, up to 17.90 PSU, also occur) [7, 8].

In the northeastern part of the sea, river waters entering the sea form mesoscale structures (plumes) adjacent to river mouths, distinguished by reduced salinity and a temperature different from the surrounding water. Their waters, as a rule, contain a large amount of suspended matter, dissolved organic matter, and nutrients [9]. River runoff entering the sea alters the chemical composition of its waters [10]. The area where river waters flow into the sea, sometimes called the marginal filter zone, acts as a "trap" for sedimentary material of natural and anthropogenic origin [11]. At its boundary, the ionic composition of the water undergoes metamorphization. As a result, the composition of the Black Sea water differs from that of the World Ocean by an increased relative content of carbonate ions and higher alkalinity [5], as well as an increased content of sulfate ions [1]. Ionic anomalies in Black Sea areas can reach: up to 1% for sulfates, up to ~ 30% for calcium ions, and up to 300–600% (3–6 times higher) for bicarbonates [12].

About 1,000 large and small rivers flow into the Black Sea. The total annual river runoff volume is ~ 350 km^3, which exceeds the input from atmospheric precipitation (238 km^3 per year) and approaches the evaporation rate (396 km^3 per year) [13]. The catchment area of ten major rivers, such as the Danube, Dnieper, Rioni, Dniester, etc., exceeds 10,000 km^2 and accounts for 80% of the total [14]. Small and medium-sized rivers contribute from 40 to 120 km^3 of the annual runoff [9]. In the northeastern Black Sea region of the Russian Federation, the large rivers Shakhe and Mzymta, several medium rivers (Pshada, Vulan, Tuapse, Psezuapse, Sochi), and more than 20 small rivers empty into the sea. The total mean long-term runoff volume into the Black Sea from the territory of Russia is about 7 km^3 per year [15]. Although the contribution of these rivers to the overall water balance of the sea is relatively small, it influences the land–sea system on a regional scale. It affects the bioproductivity of the Russian Black Sea shelf, water quality, and the level of terrigenous and anthropogenic pollution [9].

The mineralization of most Black Sea rivers (especially large rivers of the northeastern part of the sea) is substantially higher than the global average and varies within 150–600 mg/L. Their waters flow through densely populated regions with developed industry and agriculture. The concentrations of almost all MIC components in these rivers are 3–5 times higher than the global average [11]. The rapid growth of coastal cities and resort facilities, as well as agricultural activities on the coast, leads to an increase in negative impacts on aquatic ecosystems. Small rivers flowing into the northeastern Black Sea shelf, together with stormwater runoff and domestic wastewater collectors, are the main sources of most pollutants entering the marine environment. This is especially relevant near large cities – Anapa, Novorossiysk, Gelendzhik, Tuapse and Sochi [16].

Physical properties of seawater, such as salinity and density, are of fundamental importance in oceanography. They are necessary for determining seawater quality, monitoring its biogeochemical parameters, studying thermohaline circulation, and modeling water mass dynamics. The accuracy of physical parameter determination is especially important in the development of hydrophysical equipment [17, 18]. To address this, the international thermodynamic equation of seawater TEOS-10 (Thermodynamic Equation of Seawater – 2010) was developed. It takes into account changes in the relative content of dissolved inorganic components in the ocean caused by small ionic variations. However, inland seas are influenced by biogeochemical processes, and the complex spatiotemporal changes in MIC in these seas have been insufficiently studied. The applicability of modern methods for calculating physical parameters in such water bodies requires clarification.

It is known that in the open ocean, the absolute salinity deviation can be up to 0.03 g/kg, and in some coastal areas, up to 0.1 g/kg [19]. In inland seas, water areas, and estuaries, where the influence of river salts and suspended matter transported by river runoff leads to changes in the chemical composition of waters, this deviation can be much larger [10, 20]. At the same time, each sea has its own specific features, and the role of different sources of sedimentary material supply (river runoff, aeolian material, coastal abrasion, ice runoff, and others) can vary significantly in different seas [11]. Each major ion supplied by river runoff should be considered individually, since its sources, sinks, and regulators, both natural and anthropogenic, are different [21].

The MIC components supplied by river runoff are actively redistributed along the coast under the influence of hydrodynamic processes. The Northeastern Caucasian Current, which is the northeastern branch of the main cyclonic current of the Black Sea, sometimes approaches very close to the narrow shelf, leading to the formation of topographically generated cyclonic eddies. These eddies promote intense transport of trapped water along and across the shelf, enhancing the self-purification effect of the coastal zone [22], as well as the transport of MIC components.

Studying the MIC broadens the understanding of coastal water dynamics and their interaction with the environment. It must be taken into account when calculating physical properties and assessing water quality, as well as when monitoring and preventing adverse consequences of environmental changes in the region. However, the MIC of the northeastern Black Sea shelf has been insufficiently studied. Historical data for the 1964–1982 observation period are provided only in a monograph from 1992 [3]. Studies of the relationship between MIC and physical properties and the assessment of its influence on the accuracy of salinity calculation in the northeastern part of the sea had not been conducted before 2022.

The purpose of the work is to study the MIC in one of the most biogeochemically complex areas of the Black Sea – the coastal zone of the northeastern Black Sea shelf – and to assess the influence of MIC on the accuracy of salinity determination by classical and modern methods.

Materials and methods

Sampling. Water samples were collected in the northeastern Black Sea (Krasnodar Krai) at the following localities: Anapa, the settlement of Kabardinka, Novorossiysk, Gelendzhik (Golubaya and Gelendzhik bays), the villages of Divnomorskoye, Arkhipo-Osipovka, Lermontovo, the city of Tuapse, and the settlement of Lazarevskoye, in September 2022, June, September and December 2023, August 2024, and also in March and August 2025 (Fig. 1).

The samples were placed in airtight disposable 1.5 L containers and delivered to the laboratory for analysis. First, the carbonate ion content, total alkalinity (AT), and pH were determined. Then the samples were filtered through a membrane filter with a pore size of 0.45 μm to remove suspended matter and placed in 300 mL borosilicate glass containers. The samples were stored in a refrigerator at 4°C and taken out as needed during the analysis.

Salinity determination. Salinity was determined in three ways: by the sum of major ions (SS), by chlorinity (S_{Cl}), and by density (SA_{ρ}) using the TEOS-10 thermodynamic equation. To calculate the sum of ions (SS), direct laboratory chemical determinations of the concentrations of major seawater components were carried out. This method is considered the most reliable for determining salinity [23].

When calculating salinity using the chlorinity coefficient (S_{Cl}), the relationship from [1], which has been used in oceanographic practice for more than 40 years, was applied:

$$S = 1.813 \cdot \mathrm{Cl}.$$

Absolute salinity was calculated from the density values obtained in the laboratory using the TEOS-10 thermodynamic equation:

$$SA = SR + \delta SA,$$

where SA is absolute salinity (in this work denoted as SA_{ρ}), g/kg; SR is reference salinity; δSA is a regional correction, which is not constant in different seas [1]. The δSA values were estimated from the difference between the measured density of the seawater sample and the density calculated using the TEOS-10 equation of state ($\Delta\rho$) for the same reference values of salinity, temperature, and pressure. For our calculations, the algorithm most consistent with the available water density data was chosen:

$$\delta S\mathrm{A} = \Delta\rho \,/\, 0.75179,$$

where 0.75179 is the haline contraction coefficient of seawater. Other TEOS-10 algorithms requiring data on practical salinity or the carbonate system and macronutrient concentrations were not applied due to the lack of corresponding measurements.

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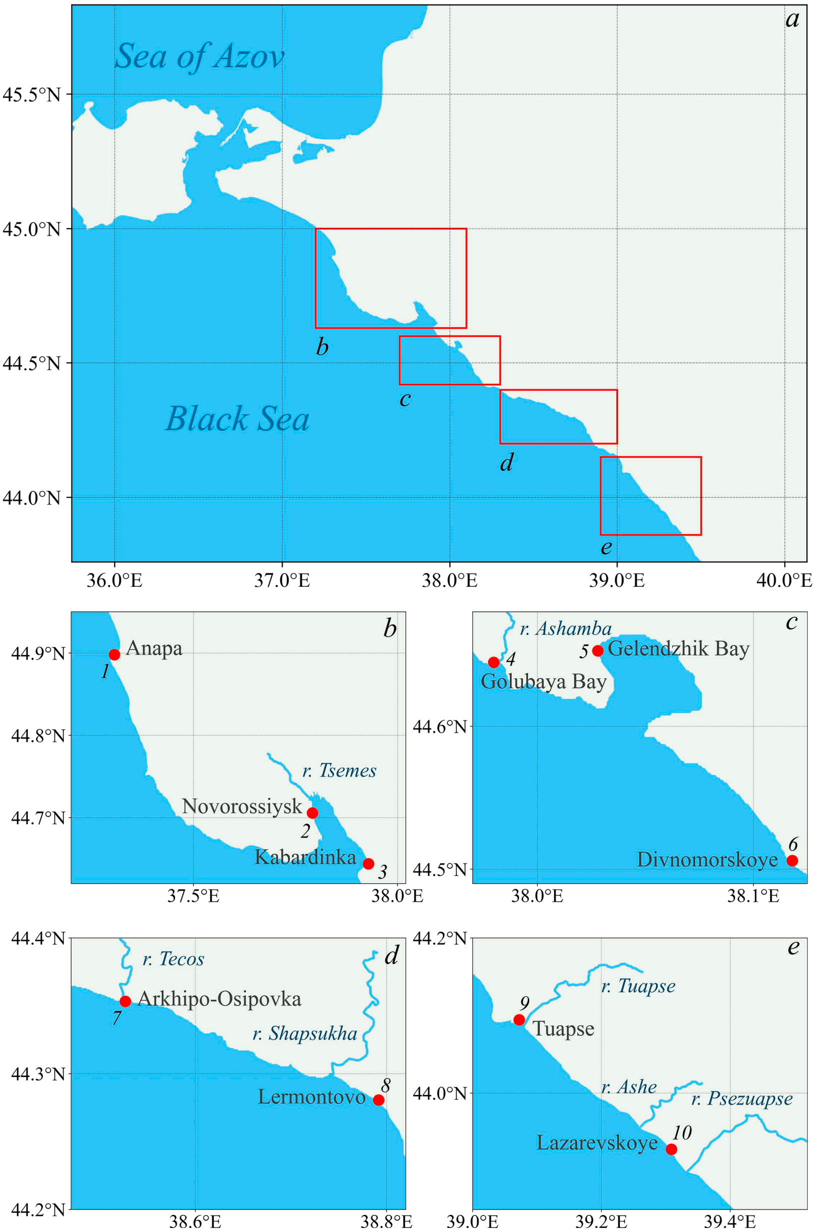
[1] TEOS-10. *Thermodynamic Equation of Seawater – 2010*. [online] Available at: http://www.TEOS-10.org [Accessed: 10 April 2026]; [online] Available at: https://www.teos-10.org/software.htm [Accessed: 10 April 2026].



F i g. 1. Location of sampling stations in 2022–2025

For oceanic water with a constant ionic composition, the accuracy of salinity calculation depends on the errors of equipment and methods and is estimated using density to be up to ±3×10^{-6} g/cm³, which is equivalent to a salinity error of ±0.4 × 10^{-2} g/kg, by chlorinity to ±0.2 × 10^{-2} g/kg, and by the sum of ions to ±0.1 × 10^{-1} g/kg [23], or ~ 0.3%.

However, in some inland water bodies and marine areas, the ratio of major ions can differ significantly from the oceanic one, and traditional methods of salinity determination by conductivity and by chlorinity prove less accurate than based on the sum of ions [4].

Seawater salinity is the total amount of solid mineral substances (salts) in grams per 1 kg of seawater. Dissolved salts in water dissociate into ions – anions (chlorides, sulfate, bicarbonate) and cations (sodium, potassium, magnesium, calcium, etc.). Direct determinations of the concentrations of these ions allow their sum, i.e., seawater salinity in grams per kilogram, to be obtained. All other methods of salinity determination are indirect and depend on various factors, among which the ratio of major ions plays a decisive role.

Despite the high accuracy of salinity values obtained by the sum of ions in waters with anomalous ionic composition, the use of this method is very limited due to its labor intensity. Laboratory analysis requires a lot of time, a large number of reagents, and special equipment. This method cannot be applied *in situ*. Salinity determination using the TEOS-10 equation is also not widely applied, as it requires a laboratory densitometer and chemical analysis of macronutrients.

The most widely used in practice is salinity determination by conductivity using a CTD probe. Traditional CTD measurements are indispensable today in marine studies, including for assessing turbulent mass exchange in the Black Sea [16].

The deviation of salinity obtained by chlorinity (ΔS_{Cl}) or by density from the sum of ions ($\Delta SA\rho$) was determined as:

$$\Delta S_{\mathrm{Cl}} = SS - S_{\mathrm{Cl}},$$

$$\Delta SA\rho = SS - SA_{\rho}.$$

Determination of major ionic composition (MIC). The concentrations of major ions (Cl^-, SO_4^{2-}, HCO_3^-, Ca^{2+}, Mg^{2+}) were determined by the potentiometric titration method, K^+ gravimetrically, and Na^+ by calculation method (as the difference between the sum of anions and cations in mole equivalents with subsequent conversion to grams per kilogram) in accordance with the methods described in detail in [24], taking into account the mineralization of the Black Sea water. To analyze the influence of ionic composition on the physical properties of seawater, the relative contribution of ions (mass fraction) to the total mineralization of the studied samples was used.

Deionized water (conductivity ~ 0.17 μS/cm) was used for preparing reagent solutions and sample dilution. The mass of the analyzed sample was measured by weighing on Ohaus AX 423 (USA) laboratory analytical balances of first accuracy class with an error of ±0.005 g.

Density determination. Density was measured in the laboratory using an Anton Paar DMA 5000M precision densitometer (Austria) by the oscillating U-tube method. The principle is based on the precise determination of the characteristic frequency and mathematical transformation of the ratio of the oscillation period of the U-tube and a reference oscillator [2].

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[2] Anton Paar GmbH, 2010. *Operating Manual DMA 4100 M, DMA 4500 M, DMA 5000 M*. Software version: V1.70. Graz, Austria: Anton Paar GmbH, 135 p.

Results

The results of the present research are given in Table 1 below.

Table 1

Hydrochemical characteristics of water samples collected off the Black Sea northeastern coast from Anapa to Lazarevskoye in 2022–2025

Station number	pH	AT, mmol/kg	Salinity, g/kg			Anions, %			Cations, %			
			SS	S_{Cl}	SA_{P}	Cl^-	SO_4^{2-}	HCO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}
29.09.2022												
1	8.11	3.05	19.00	18.67	18.87	54.21	7.95	0.93	31.40	1.26	1.20	3.06
2	7.93	3.08	17.70	17.32	17.62	53.98	7.98	1.08	31.44	1.34	1.23	2.95
4	8.08	3.11	18.89	18.59	18.68	54.33	7.76	0.96	31.49	1.29	1.11	3.05
5	8.15	3.05	18.59	18.20	18.46	54.01	8.02	1.01	31.45	1.36	1.18	2.98
7	8.01	3.07	18.90	18.55	18.77	54.14	7.93	0.98	31.51	1.25	1.19	2.99
9	8.03	3.07	18.67	18.34	18.70	54.20	7.86	0.99	31.49	1.26	1.23	2.98
10	7.97	3.11	18.36	18.06	18.22	54.26	7.79	1.02	31.54	1.20	1.20	3.00
Average	**8.04**	**3.08**	**18.59**	**18.25**	**18.47**	**54.16**	**7.90**	**0.99**	**31.47**	**1.28**	**1.19**	**3.00**
Δm	***0.22***	***0.06***	***1.30***	***1.35***	***1.25***	***0.35***	***0.26***	***0.15***	***0.14***	***0.16***	***0.12***	***0.11***
27.06.2023–29.06.2023												
1	8.20	2.95	18.35	18.10	18.28	54.42	7.99	0.95	30.44	1.27	1.39	3.54
2	8.45	3.10	18.10	17.85	17.95	54.40	7.99	0.98	30.43	1.30	1.34	3.56
5	8.20	3.30	15.05	14.73	14.88	53.97	8.17	1.31	30.28	1.22	1.54	3.51
7	8.15	3.05	16.79	16.58	16.84	54.46	7.82	1.12	30.44	1.19	1.42	3.55
9	8.23	3.02	12.61	12.29	12.42	53.76	8.35	1.43	29.87	1.25	1.77	3.58
10	8.25	2.78	15.24	14.93	15.24	54.03	8.27	1.13	30.29	1.28	1.48	3.53
Среднее / Average	**8.25**	**3.03**	**16.02**	**15.75**	**15.93**	**54.17**	**8.09**	**1.15**	**30.29**	**1.25**	**1.49**	**3.55**
Δm	***0.30***	***0.52***	***5.74***	***5.81***	***5.86***	***0.70***	***0.53***	***0.48***	***0.57***	***0.11***	***0.43***	***0.07***
13.09.2023–14.09.2023												
1	8.35	3.13	18.55	18.29	18.31	54.39	7.91	0.98	30.58	1.30	1.45	3.39
2	8.89	3.07	18.37	18.19	18.19	54.62	7.86	0.83	30.42	1.26	1.54	3.47
3	8.39	3.21	18.36	18.09	18.29	54.35	7.97	1.02	30.45	1.27	1.47	3.47
4	8.45	3.20	18.30	18.07	18.14	54.45	7.92	0.98	30.41	1.26	1.48	3.50
7	8.34	3.09	18.00	17.73	17.84	54.35	7.91	1.06	30.52	1.28	1.46	3.42
8	8.34	3.22	17.85	17.61	17.81	54.40	7.92	1.04	30.33	1.30	1.52	3.50
9	8.46	3.07	18.42	18.19	18.26	54.49	7.86	0.98	30.42	1.29	1.48	3.48
10	8.34	3.22	18.34	18.10	18.16	54.43	7.92	0.96	30.47	1.23	1.59	3.40
Average	**8.45**	**3.15**	**18.27**	**18.03**	**18.13**	**54.44**	**7.91**	**0.98**	**30.45**	**1.27**	**1.50**	**3.45**
Δm	***0.55***	***0.15***	***0.70***	***0.68***	***0.5***	***0.27***	***0.11***	***0.23***	***0.25***	***0.07***	***0.14***	***0.09***
05.12.2023–07.12.2023												
2	8.22	2.36	17.88	17.38	–	53.61	8.91	0.86	30.28	1.40	1.45	3.48
3	8.33	2.41	18.59	18.08	–	53.64	9.00	0.83	30.12	1.34	1.47	3.59
4	8.44	1.65	8.77	7.90	–	49.67	12.88	1.24	30.12	1.24	1.58	3.26
7	8.23	2.43	18.69	18.18	–	53.64	8.92	0.85	30.34	1.32	1.43	3.50
9	8.21	2.33	18.44	17.89	–	53.52	9.11	0.84	30.33	1.27	1.40	3.54
Average	**8.29**	**2.24**	**16.47**	**15.89**	**–**	**52.82**	**9.76**	**0.92**	**30.24**	**1.31**	**1.47**	**3.48**
Δm	***0.23***	***0.78***	***9.92***	***10.28***	***–***	***3.97***	***3.97***	***0.41***	***0.21***	***0.16***	***0.18***	***0.33***
10.08.2024												
4	8.17	2.78	18.96	18.42	18.25	53.59	8.83	0.94	30.52	1.33	1.39	3.40

Table 1 (concluded)

Station number	pH	*AT*, mmol/kg	Salinity, g/kg			Anions, %			Cations, %			
			SS	S_{Cl}	SA_{ρ}	Cl^-	SO_4^{2-}	HCO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}
04.03.2025												
1	7.93	3.18	18.96	18.38	18.74	53.96	8.48	0.98	30.33	1.28	1.42	3.55
27.08.2025–29.08.2025												
4	8.60	3.13	19.06	18.19	18.70	52.63	10.02	0.97	30.25	1.23	1.29	3.61
5	8.56	3.28	19.28	18.39	18.97	52.62	10.02	0.96	30.29	1.20	1.31	3.58
6	8.58	3.32	18.99	18.29	18.85	53.12	9.51	0.97	30.27	1.67	1.31	3.65
Average	**8.58**	**3.24**	**19.11**	**18.29**	**18.84**	**52.79**	**9.85**	**0.97**	**30.27**	**1.37**	**1.30**	**3.61**
Δ*m*	***0.04***	***0.19***	***0.28***	***0.20***	***0.27***	***0.50***	***0.51***	***0.01***	***0.04***	***0.47***	***0.02***	***0.07***

The number of stations in each expedition varied: in September 2022 – 7, in June 2023 – 6, in September 2023 – 8, in December 2023 – 5; in August 2024 – 1, in March 2025 – 1, and in August 2025 – 3. One sample was collected at each station.

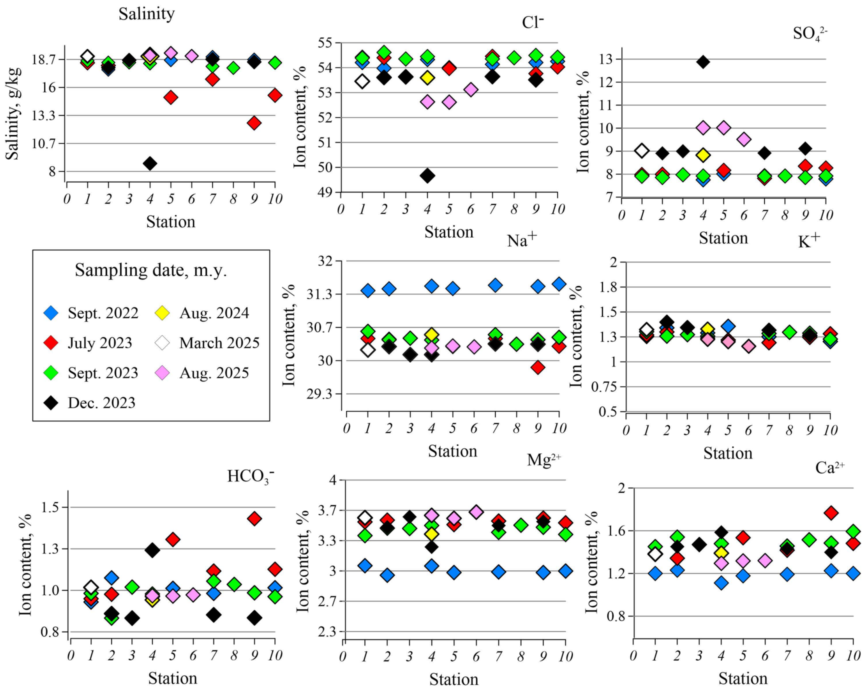
The pH values of the studied Black Sea water samples ranged from 7.90 to 8.89 (Table 1). Total alkalinity mainly varied from 2.33 to 3.30 mmol/kg, except for December 2023, when at St. *4*, in the area of the Ashamba River runoff, AT was 1.65 mmol/kg at a low water salinity (*SS* = 8.77 g/kg).

The *SS*, S_{Cl} and *SA*ρ values differ (Table 1): *SS* is the highest, while S_{Cl} is in most cases the lowest. The range (Δ*m*) serves as a measure of water mass heterogeneity for each of the determined parameters (pH, AT, salinity, relative ion content) among the stations. For example, in September 2022, September 2023, and August 2025, the alongshore water masses were almost homogeneous in salinity in the direction from Anapa to Lazarevskoye (Δ*m* = 0.2…1.3), whereas at the end of June 2023, on the contrary, a high heterogeneity was noted (Δ*m* ~ 5.8).

Fig. 2 presents the dynamics of the relative content of MIC components and salinity in 2022–2025 (according to the data in Table 1). The relative content of Cl^- in the coastal Black Sea water over the entire study period was in the range 52.6–54.6%, SO_4^{2-} – 7.8–12.9%, HCO_3^- – 0.8–1.4%, Na^+ – 29.9–31.5%, Ca^{2+} – 1.1–1.8%, and Mg^{2+} – 3–3.7%. The content of SO_4^{2-}, HCO_3^-, and Ca^{2+} in the MIC varied almost twofold, which is associated with substantial freshening and, possibly, contamination of seawater by continental runoff.

Over the entire observation period, the *SS* of most samples averaged ~ 18.40 g/kg. The maximum value (*SS* = 19.11 g/kg) was recorded in August 2025 in the Gelendzhik Bay (St. *4*), and the minimum (*SS* = 8.77 g/kg) in December 2023 in the Golubaya Bay near the Ashamba River runoff area (St. *3*).

Fig. 2 shows that the water samples collected in September 2022 stand out markedly among all other samples. Compared to the average major ion content in the remaining samples over the entire study period, the Na^+ content was elevated by ~ 4%, while Ca^{2+} and Mg^{2+} were lowered by ~ 20% and ~ 14%, respectively. Meanwhile, the water mass was practically homogeneous from Anapa to Lazarevskoye in terms of MIC and salinity (Δ*m* was 0.1–0.4). The mean salinity of these samples was close to the average for the entire observation period (*SS* = 18.40 g/kg) and amounted to 18.59 g/kg.



F i g. 2. Sum of ions and relative content of MIC components in coastal waters of the northeastern Black Sea (in the settlements from Anapa to Lazarevskoye) in 2022–2025

Fig. 2 shows that the water samples collected in September 2022 stand out markedly among all other samples. Compared to the average major ion content in the remaining samples over the entire study period, the Na^+ content was elevated by ~ 4%, while Ca^{2+} and Mg^{2+} were lowered by ~ 20% and ~ 14%, respectively. Meanwhile, the water mass was practically homogeneous from Anapa to Lazarevskoye in terms of MIC and salinity (Δm was 0.1–0.4). The mean salinity of these samples was close to the average for the entire observation period (SS = 18.40 g/kg) and amounted to 18.59 g/kg.

The water samples collected in June 2023 were characterized by the lowest salinity of all (SS from 12.61 to 18.35 g/kg). In the MIC of the low-salinity samples, bicarbonate ions predominated (up to 1.4% at St. *9*, Tuapse). The highest content of calcium ions among all studied samples (up to 1.77%) was also observed here. At St. *5*, *9*, and *10*, the sulfate content was slightly higher than at other stations in this expedition.

In September 2023, uniformity in salinity and the ratio of major ions in the composition was observed among all water samples, similar to September 2022. The average salinity of the samples was 18.27 g/kg (Δm was ~ 0.6 g/kg), and the MIC was characterized by a higher content of magnesium and calcium cations compared to September 2022.

In December 2023, the MIC differed significantly from the MIC of samples obtained at other times, although the salinity corresponded to the average level characteristic of most studied samples and amounted to SS = 18.40 g/kg.

The SO_4^{2-}/Cl^- ratio in December 2023 was high, equal to 0.17, while the HCO_3^- content, on the contrary, was the lowest of all studied samples (~ 0.85%). An exception was the sample from St. *4* (near the Ashamba River runoff area). River waters freshened the Black Sea water to SS = 8.77 g/kg. The MIC of these waters differed significantly from the composition of all studied water samples presented in this work. The relative content of sulfates was ~ 1.4 times higher, and chlorides ~ 1.1 times lower, than in other samples obtained during the December 2023 expedition. The SO_4^{2-}/Cl^- ratio at St. *4* was 0.26, which is more typical of river waters. The HCO_3^- content at St. *4* was 1.5 times higher, and the Mg^{2+} content 8% lower, than in the other samples from this period.

In the expedition to Golubaya Bay (St. *4*) in August 2024 and to Anapa (St. *1*) in March 2025, one water sample was collected, with salinities of 18.78 and 18.96 g/kg, respectively. In the MIC of these samples, the sulfate ion content was fairly high, unlike most samples, and the SO_4^{2-}/Cl^- ratio was 0.18 and 0.17, respectively.

The content of K^+ cations was fairly stable in all studied samples: on average 1.28% (Δm was 0.05–0.16%), with the maximum value (1.40%) recorded in December 2023 at St. *2*, and the minimum in September 2022 at St. *9* (1.20%).

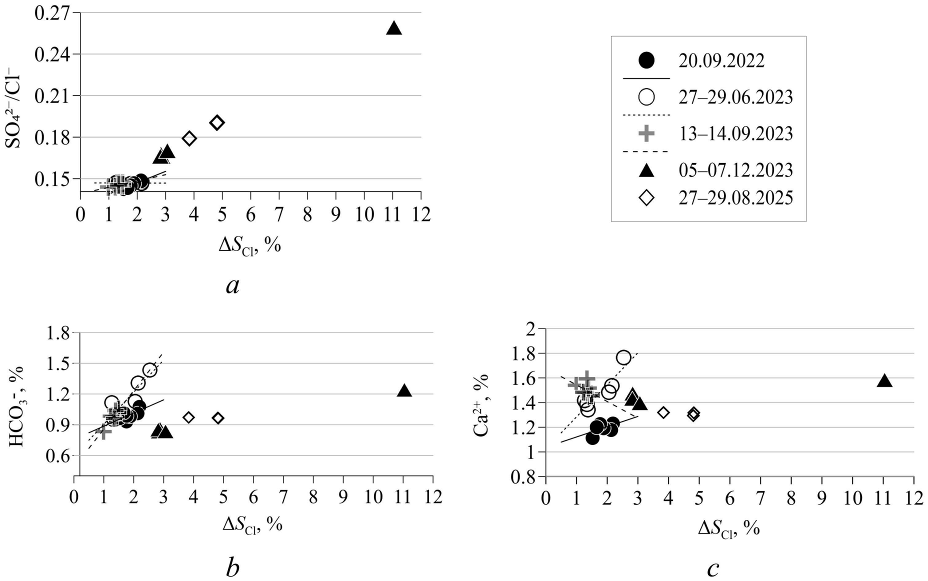
Influence of ionic composition on the physical properties of water. Fig. 3 shows the relationship between the MIC and the ΔS_{Cl} and $\Delta SA\rho$ values. During the observation period 2022–2025, ΔS_{Cl} ranged from 0.1 to 11.1%, and $\Delta SA\rho$ from 0 to 2–4% (as stated: 0–2 4% likely a typo, but it will be kept in 0–4% range based on context). In December 2023 and August 2025, an increase in ΔS_{Cl} correlated with a rising trend in SO_4^{2-}/Cl^-, whereas the HCO_3^- and Ca^{2+} contents were almost the same at the three high-salinity stations (average *SS* = 18.40 g/kg) and did not influence the ΔS_{Cl} increase. This phenomenon was observed in all water samples obtained in December 2023, except for the sample from St. *4*, where at the lowest observed salinity (*SS* = 8.77 g/kg) and a substantially different MIC from the other samples, the ΔS_{Cl} value was the largest (11.05%) and depended on all three components (SO_4^{2-}, HCO_3^-, and Ca^{2+}) simultaneously.

At the end of June 2023, the ΔS_{Cl} value reached 2.5%, with no relationship with the SO_4^{2-}/Cl^- ratio (Fig. 3, *a*). On the contrary, an increase in HCO_3^- and Ca^{2+} content correlated with a rise in ΔS_{Cl} at all stations (Fig. 3, *b* and *c*).

In September 2023, the ΔS_{Cl} values in the samples were similar, and a slight increase in ΔS_{Cl} was associated with an increase in SO_4^{2-} and HCO_3^-. No relationship was observed between the Ca^{2+} content, which was similar in all samples, and the ΔS_{Cl} increase.

Overall, over the studied period, a quite definite relationship was revealed between ΔS_{Cl} and the content of SO_4^{2-}, HCO_3^-, and Ca^{2+} in the MIC. An increase in ΔS_{Cl} was accompanied by an increase in the content of all three ions in the water composition simultaneously, as well as each individually or in pairs.

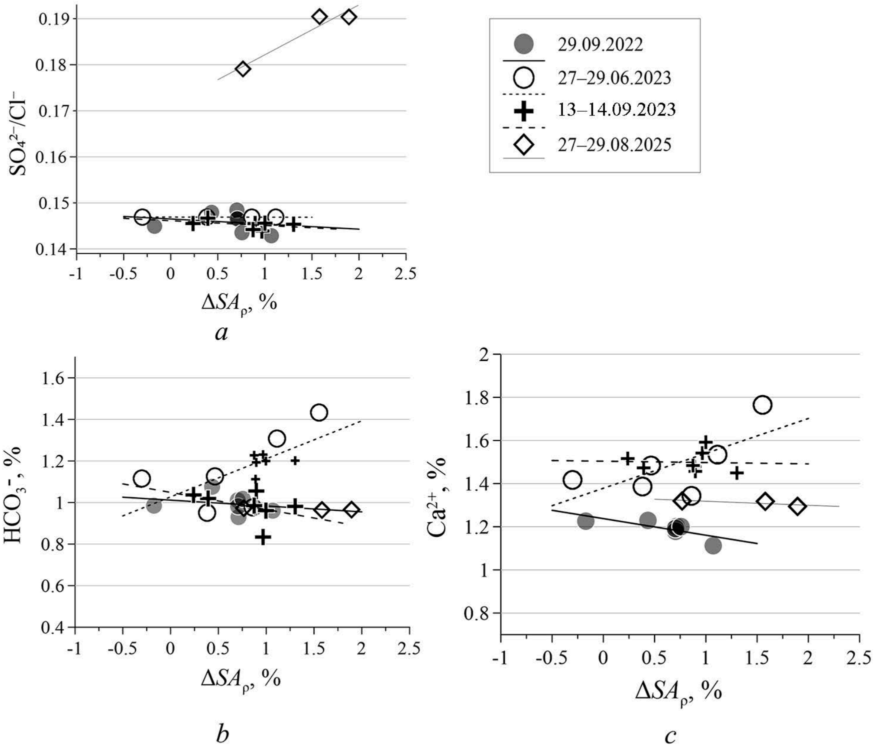
Fig. 4 presents the relationship between ΔSA_ρ and the ionic composition of the Black Sea waters. As can be seen, the dependence of ΔSA_ρ on MIC variations is ambiguous for the four expeditions. In September 2022 and 2023, no relationship was observed between an increase in ΔSA_ρ and changes in the content of SO_4^{2-}, HCO_3^-, and Ca^{2+}. In June, the rise in the ΔSA_ρ trend was accompanied by an increase in the relative content of HCO_3^- and Ca^{2+}. And in August 2025, the increase in ΔSA_ρ was accompanied by a rise in the SO_4^{2-}/Cl^- ratio.



a

b *c*

F i g. 3. Relationship between ΔS_{Cl} and relative content of SO_4^{2-} (*a*), HCO_3^- (*b*) and Ca^{2+} (*c*) in MIC of coastal waters of the northeastern Black Sea based on the data of five expeditions



a

b *c*

F i g. 4. Relationship between ΔSA_{ρ} and relative content of SO_4^{2-} (*a*), HCO_3 (*b*) and Ca^{2+} (*c*) in MIC of coastal waters of the northeastern Black Sea based on the data of four expeditions

Unfortunately, the density of water samples from the December 2023 expedition could not be determined; therefore, ΔSA_ρ was not calculated for them.

Thus, an explicit relationship between ΔSA_{ρ}` and the MIC was observed only for the water samples collected in June 2023, i.e., for samples with salinity substantially lower relative to the average, and the increase in ΔSA_ρ depended on the rise in the relative content of HCO_3^- and Ca^{2+} in the water MIC.

Discussion

The movement of water masses, river runoff inflow, and biogeochemical processes in the coastal zone lead to seasonal variations in the physicochemical properties of seawater. When river and sea waters mix, the behavior of almost all chemical elements changes significantly. Seawater exerts a dissolving effect on some of them, while others, on the contrary, sharply lose geochemical mobility and precipitate [11, 25]. The composition of terrigenous material at the river–sea geochemical barrier changes substantially. For example, ~ 80% of exchangeable calcium is replaced mainly by sodium and, to a lesser extent, by magnesium and potassium [26].

A comparative analysis revealed significant spatiotemporal variability of salinity and the relative content of MIC components in the coastal waters of the northeastern Black Sea shelf. The causes of these changes are different; therefore, to understand them, each expedition must be considered separately. Fig. 2 presents an analysis of the change in water salinity (*SS*) during 2022–2025 separately for each station (based on the data from Table 1). The lowest sum-of-ions values were recorded in water samples collected in June 2023 at stations from Gelendzhik to Lazarevskoye, ranging from 12 to 18 g/kg. The water freshening in the coastal zone was most likely caused by heavy rainfalls that overfilled the runoff of mountain rivers into the sea. Mountain river runoff was present near practically every locality where water samples were collected (see Fig. 1). The presence of river waters in the samples obtained in June 2023 is confirmed by the elevated relative content of HCO_3^- in samples from *St*. 5, 7, 9, and 10, and SO_4^{2-} at St. 5, 9, and 10. The elevated Ca^{2+} and lowered Na^+ content in the sample from *St*. 9 (Tuapse) indicates active sorption-desorption processes characteristic of the river–sea area [10]. Most rivers in the northeastern part of the sea discharge more than 80% of their runoff in the winter-spring period, which is associated with the predominance of the rain-fed component in their nutrition [27]; however, powerful rainfalls are also characteristic of this region in the summer, often causing floods [28]. The maximum content of ions usually predominating in river runoff (HCO_3^-, SO_4^{2-}, and Ca^{2+}) and the minimum content of ions characteristic of marine waters (Cl^-, Na^+) indicate the dominance of river waters in the samples. In all likelihood, the source of these waters in June 2023 was the Tuapse River, which is formed by the confluence of two mountain rivers and flows into the sea near the city of Tuapse, not far from the sampling site. The Tuapse River basin is located in a semi-humid subtropical zone and is the most mudflow-prone of all rivers on the Black Sea coast of Russia. Floods occur here at any time of the year (except August, September, and October) due to abundant precipitation. The water level in the rivers can rise by 6–8 m [29].

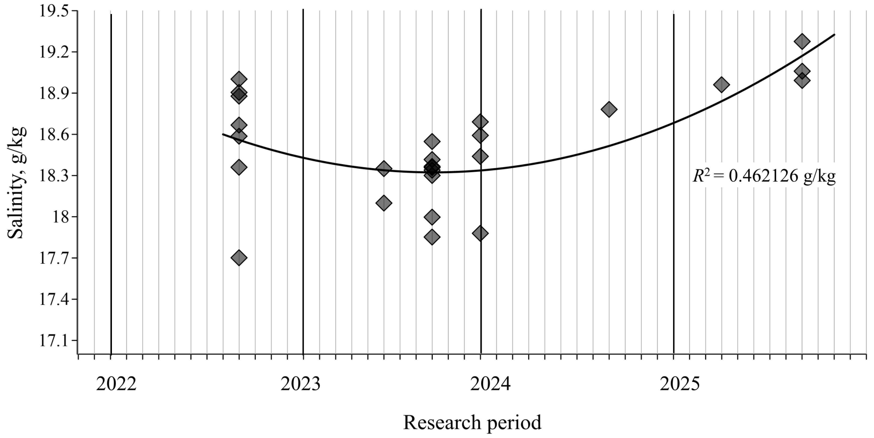
In December 2023, the very low salinity for Black Sea waters (*SS* = 8.77 g/kg) in Golubaya Bay at St. *4* was caused by abundant runoff from the small (12 km) Ashamba River. Its source is in the mountains, and the runoff volume depends significantly on precipitation. During floods, the water level in the river rises sharply [30], and river runoff into the sea intensifies. As the December 2023 studies showed, river runoff transforms the MIC of seawater towards an increase in the relative content of SO_4^{2-} and HCO_3^- and a decrease in Mg^{2+} content.

A prolonged absence of intense precipitation and moderate river runoff promote the inflow of waters from the open sea into coastal zones, while the MIC and salinity along the northeastern coast level out, and a uniform water mass is formed. It can be assumed that until mid-September 2022, there had been no abundant precipitation capable of provoking intense river runoff into the sea for a long time; therefore, the water along the coast from Anapa to Lazarevskoye was closest in composition to the waters of the open sea. Table 2 compares the averaged values of the relative content of MIC components for the water masses observed in September 2022 and 2023 from Anapa to Lazarevskoye, as well as for the water mass whose samples were obtained in September 2022 along the route of the SRV *Ashamba* from Golubaya Bay towards the Kerch Strait at ~ 10 km from the coast (according to the data from [24]).

Table 2

Major ionic composition of water masses off the Black Sea northeastern coast from Anapa to Lazarevskoye, and from Gelendzhik to the Kerch Strait as compared to the SSW characteristics

Sampling area	Date	Salinity, g/kg	Anions, %			Cations, %				Source of data
			Cl^-	SO_4^{2-}	HCO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	
Anapa – Lazarevskoye (Sochi)	September, 2022	18.59	54.16	7.90	0.99	31.47	1.28	1.19	3.00	[12]
	September, 2023	18.27	54.43	7.91	0.98	30.45	1.27	1.50	3.45	Present study
Gelendzhik – Kerch Strait	September, 2022	18.75	54.23	8.21	0.99	30.33	1.25	1.39	3.59	[12]
Atlantic Ocean (SSW)	–	35.17	55.07	7.82	0.35	30.82	1.22	1.19	3.53	[2]



F i g. 5. Trend of salinity change in 2022–2025

Fig. 5 shows the interannual variability of salinity in the coastal waters of the northeastern Black Sea shelf. It is depicted by a solid line of a second-degree polynomial, the coefficients of which were fitted by minimizing the standard deviation from the obtained data. Over the four years of research (2022–2025), a tendency towards increasing salinity is observed in the coastal waters. It has become known earlier that the physical and biogeochemical properties of the Black Sea water column change over time under the influence of natural and anthropogenic causes. The air and sea surface temperature, as well as water salinity, have increased over the past 40 years, while ice cover and the freshwater input component of the water balance have decreased [31]. It has been found that in the last decade, the increase in practical salinity in the upper 200-m layer of the sea is about 0.05–0.06 PSU per year. This changes the water density and may affect the position of the lower boundary of the oxygen-containing layer [32]. Along with the listed causes, an additional contribution to the increase in coastal water salinity in the Black Sea, especially in resort areas, may be made by polluted continental runoff. However, due to the limited amount of data and the short observation period, this assumption requires confirmation by additional research.

Historical data on salinity obtained by the sum of ions in the region of the northeastern Black Sea shelf are almost impossible to find in literature sources. Since the end of the 20th century, it has been considered that the salinity of surface waters of the sea generally varies from 17.5 g/kg to 18.3 g/kg [5]. In [1], the salinity of surface waters in the eastern part of the sea is indicated (18.10 and 18.54 g/kg). The 1992 monograph mentions salinity in the eastern part of the sea in November 1977 as 18.50 g/kg, and in March 1986 as 18.09 g/kg [3]. The results of this study show that modern salinity exceeds the historical values.

To assess the differences between the Black Sea waters and oceanic water, the relative MIC of standard seawater (SSW) is given in Table 2. It shows that the salinity of the water masses in the northeastern Black Sea is almost two times lower than that of SSW, and their relative MIC, due to the presence of river and Azov Sea waters, differs significantly from the SSW composition and exhibits spatiotemporal variability. Despite the variability of the Black Sea water mass MIC, the averaged composition (without intense runoff influence) contains ~ 1% less chlorides and ~ 0.4% less Na^+ in most cases, but ~ 0.1% more sulfates, ~ 0.3% more calcium ions, and approximately three times more bicarbonates than SSW. The input of continental runoff increases the relative content of HCO_3^-, Ca^{2+}, and SO_4^{2-} in the MIC of marine waters.

During this research, the spatiotemporal variability of the hydrochemical properties of coastal water masses in the area of the northeastern Black Sea shelf, mainly associated with the presence or absence of river runoff, was discovered, and its assessment was carried out. In August 2025, a significant increase in the SO_4^{2-}/Cl^- ratio was observed in the absence of a substantial influence of river runoff. Sulfates enter the Black Sea, as well as the ocean, from various sources: with products of volcanic activity, during the decomposition of organic matter by bacteria in deep layers and at the bottom of the water body, with river waters during rock dissolution, and from the air. In addition, SO_4^{2-} is supplied from the Mediterranean Sea, and a significant amount also results from economic activities with polluted continental runoff [3, 33–35]. August is the peak of the holiday season on the coast of Krasnodar Krai, and precipitation is generally absent at this time. Therefore, the increase in sulfates in the water MIC may be associated with the discharge of a large volume of domestic wastewater into the sea. Assessment of the impact of wastewater on the MIC requires additional research. HCO_3^- and Ca^{2+} usually enter the sea with river runoff, as a result of redissolution of bottom sediments, and other processes.

MIC determines the seawater salinity. Calculating salinity in such a complex environment as the coastal part of the northeastern Black Sea shelf is a challenging task. Earlier studies have shown that deviations when calculating salinity by various methods, for example, in the Kerch Strait, can reach: by conductivity (CTD probe) and by chlorinity – up to 3%, by density – up to 2%, and in bays and lagoons – even more [4, 12]. The maximum deviation values in our data were much higher: when calculating salinity by water chlorinity (ΔS_{Cl}) in the coastal waters of the northeastern Black Sea shelf, it amounted to ~ 5% (in August 2025) and 11% (at the river mouth in December 2023), and by density (ΔSA_ρ) ~ 4% (in August 2024). Since salinity is closely related to MIC variations, none of these methods yields an accurate result. The TEOS-10 equation does not take into account the influence of the additional amount of all macronutrients supplied from external sources (for example, sulfates). Its application in the coastal waters of the Black Sea can only be used to obtain an approximate estimate of water salinity within the limits of the observed deviations. Furthermore, elevated nutrient content also affects the accuracy of salinity calculation using TEOS-10 in inland seas [34]. Comparison of the obtained results with similar studies [4, 12] showed that the freshening of coastal waters on the northeastern shelf during periods of intense river runoff is more significant, and the errors in salinity calculation by chlorinity and by density are larger than, for example, in the Kerch Strait.

As the results of our study have shown, the most accurate salinity values for the coastal waters of the Black Sea at present can only be obtained by the sum of ions. Other methods can only provide approximate estimates.

Conclusions

In the course of the research, new hydrochemical data on the coastal waters of the northeastern Black Sea shelf from Anapa to Lazarevskoye (Sochi) for the 2022–2025 observation period were obtained. Significant spatiotemporal variability of salinity and the major ionic composition of the waters was discovered. Over the studied period, the relative ion content in the water composition was: Cl^- – 52.6−54.6%, SO_4^{2-} – 7.8−12.9%, HCO_3^- – 0.8−1.4%, Na^+ – 29.9−31.5%, Ca^{2+} – 1.1–1.8%, and Mg^{2+} – 3−3.7%. The content of SO_4^{2-}, HCO_3^-, and Ca^{2+} varied almost twofold. Preliminary results indicate a trend towards increasing salinity over time in the coastal waters of the northeastern Black Sea shelf. The causes of salinity and MIC fluctuations are variable river runoff and, possibly, the discharge of domestic wastewater.

A comparison of three methods for determining salinity – by the sum of ions (SS), by the chlorinity coefficient (S_{Cl}), and by density using the TEOS-10 equation (SA_ρ) – was carried out. The most accurate of these methods for the Black Sea waters is the calculation by the sum of ions. This conclusion is probably valid for water bodies of a similar type as well.

A relationship was found between the increase in salinity determined by chlorinity and the increase in the content of SO_4^{2-}, HCO_3^-, and Ca^{2+}. When calculating salinity by water density, no such relationship was observed.

The deviations of the chlorinity-based salinity calculation from the sum of ions reached 5% (at SS = 19 g/kg), or 0.9 g/kg, in the coastal seawater, and 11% (at SS = 9 g/kg), or 0.9 g/kg, directly at the river mouth; and the deviation of the density-based salinity calculation using the TEOS-10 equation in coastal seawater with a salinity of 19 g/kg reached 4%. Comparison of the obtained data with earlier results showed that the freshening of marine waters in the coastal part of the northeastern Black Sea shelf can be more pronounced, and the maximum deviations in salinity calculation larger, than, for example, in the waters of the Kerch Strait.

The advantage of using the method proposed by the authors for determining salinity by MIC or sum of ions consists not only in improving the accuracy of the salinity results obtained, but also in the possibility of identifying the causes of its change due to seasonal variations in the content of certain ions (SO_4^{2-}, HCO_3^-, and Ca^{2+}) in coastal waters. A significant drawback of the method remains its labor intensity and long duration.

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