

Sulfate-Chlorinity Ratio in the Black Sea Water and its Variability over the Last 70 Years

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Abstract

Purpose. Microbial reduction of sulfate in the anoxic basins leads to a non-conservative behavior of sulfate relative to chlorinity. Sulfate deficiency indicates its consumption and a weak process of water renewal. The sulfate-chlorinity ratio has been repeatedly studied in the Black Sea waters, its 3% deficit was revealed in deep waters in the 1950s. In the light of possible impact of climate change on the water balance of the Black Sea, modern variations in the sulfate-chlorinity ratio are considered and compared with the results of the studies in the 20th century.

Methods and Results. Chlorinity was obtained by potentiometric titration with AgNO_3 solution. Sulfates were measured gravimetrically after BaSO_4 precipitation from two parallel seawater samples at the stations on the slope and in the center of the sea. The IAPSO seawater standard (Practical Salinity 34.993; Batch P162) was used as a reference sample. Chlorinity increases with depth from 9.77 to 12.32 g/kg with a change in conductometric salinity from 17.72 to 22.33. Sulfate concentration increases from 14.45 mmol/kg at the surface to 17.47–17.52 mmol/kg at the 200–600 m depths, at the bottom it decreases to 17.44 mmol/kg. The relationship between the sulfate concentration and chlorinity is linear up to chlorinity 12 g/kg, below 200 m sulfate concentration does not depend on chlorinity. The sulfate-chlorinity ratio on the sea surface is 0.1420 g/g. It monotonically decreases up to the depth 1200 m where it reaches its minimum value 0.1353 g/g. Below 1200 m, the SO_4/Cl value varies within a small range from 0.1356 to 0.1361.

Conclusions. Comparison of data on chlorinity and sulfate concentration over the last 70 years (1952–2021) shows that within the precision of the analyses performed, chlorinity and sulfate concentration remain constant that reflects a stationary character of the Black Sea system over this period.

Keywords: sulfate, chlorinity, sulfate-chlorinity ratio, sulfate reduction, Black Sea

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Salinity is a fundamental characteristic of the ocean and sea water masses. 86% of the salt component consists of Na^+ and Cl^- ions, the rest is represented by $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ cations in descending order and $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{Br}^- > \text{F}^-$ anions [1]. The ratio of the principal sea water cations and anions changes little, and in hydrophysical studies, salinity is determined by the electrical conductivity method. The relationship between the composition of sea water and salinity, obtained from electrical conductivity, is expressed by the formula for the sulfate-chlorinity ratio $S = 1.80655 C/\text{‰}$. Chlorinity is understood as the sum of halogen ions ($\text{Cl}^- + \text{Br}^- + \text{I}^-$), expressed as the silver equivalent precipitated during titration of sea water solutions with a silver nitrate solution. Elements behave conservatively in a sea water solution if their ratio to chlorine does not change with salinity change.



In oxygen-containing water, sulfate behaves conservatively relative to chlorinity. Under anaerobic conditions, sulfate is consumed in the processes of microbial sulfate reduction (works ^{1,2} and [2]), and therefore its behavior with respect to chlorinity may not be conservative.

Based on the water balance, the only source of salt in the Black Sea is the lower Bosphorus current with a salinity of 35–37. In the Black Sea water column, salinity increases with depth from 17–18 on the surface to 23.3 in the bottom convective layer (work ³ and [3–5]). Halogens (Cl⁻ and Br⁻) in the sea water composition do not participate in oxidation-reduction reactions and therefore can serve both as an indicator of changes in salinity and a conservative sea water component. Iodine concentration in the Black Sea water is too low (< 50 ng/g) and does not have a significant effect on the chlorinity value within the measurement error.

The paper ³ presents data obtained in 1931, which shows that the chlorine coefficient (the salinity to chlorinity ratio) for the upper water column of the Black Sea differs from the oceanic one and equals 1.813. After analyzing 122 samples in the Black Sea water (taken during the R/V *Atlantis II* expedition in 1969), K. Kremling [6] concluded that the conductometric salinity to chlorinity ratio is described by the formula $S‰ = 1.813 Cl‰$.

Sulfate does not behave conservatively in the anaerobic zone of the Black Sea, undergoing reduction in the water column. Back in the 50s of the past century, it was shown ^{1,2} that the sulfate-chlorinity ratio decreases with depth from 0.1410 to 0.1362 g/g. The authors attributed this change to the microbial reduction of sea water sulfate.

At the end of the 60s a study of the sulfate concentration at station 1486 was carried out [6]. Data on the sulfate-chlorinity ratio obtained in 1985–1989 is presented in [2, 7]. Minimum values of the sulfate-chlorinity ratio in the Black Sea water were slightly different in these works (0.134 [6] and 0.137 [2, 7]). However, the general pattern of the sulfate-chlorinity ratio decrease with depth was fully confirmed. Based on the study of the sulfur isotope composition of seawater sulfate, it was shown that a decrease in the sulfate-salinity ratio with an increase in salinity with depth is accompanied by the increase of $\delta^{34}S(SO_4)$ value from +21‰ at the surface to +23‰ at the bottom water relative to the VCDT standard (Vienna Canyon Diablo Troilite) [8–11]. Such fractionation of sulfate sulfur isotopes is possible as a result of microbial sulfate reduction. Despite the abundance of determinations of salinity by electrical conductivity from 1993 until present, the data on chlorinity and sulfate concentration in the Black Sea water hasn't been found.

The aim of the present paper is to consider the change in sulfate concentration in the Black Sea water column relative to chlorinity both in its central part and in the continental slope area. Based on the results presented, the zonation of sulfate changes in the water column will be shown. Using the data given in works ^{1,2}

¹ Skopintsev, B.A. and Gubin, F.A., 1955. [Some Results of Hydrochemical Investigations in the Black Sea in 1952-1953]. In: *Trudy Morskogo Gidrofizicheskogo Instituta AN SSSR* [Proceedings of the Marine Hydrophysical Institute of AS USSR]. Moscow: AS USSR Publ. Vol. 5, pp. 71-98 (in Russian).

² Skopintsev, B.A., 1975. [*Formation of the Modern Chemical Composition of the Black Sea Waters*]. Leningrad: Gidrometeoizdat, 336 p. (in Russian).

³ Bruevich, S.V., 1953. Chemistry and Biological Productivity of the Black Sea. In: *Trudy Instituta Okeanologii AN SSSR*. Moscow: Akademia Nauk SSSR. Vol. 7, pp. 11-56 (in Russian).

[2, 6, 7], the sulfate-chlorinity ratio evolution in the Black Sea water over the past 70 years of observations will be considered.

Materials and methods

Chlorinity and salinity were measured at two stations Ash-23 and Ash-25 in samples taken on July 9 and 14, 2021, respectively, at a point 44° 29.34'N, 37° 52.14'E located seven miles from the coast (continental slope area, the depth of 1200 m (Fig. 1)). Sampling was carried out during the Black Sea 2021 expedition with six 4-liter plastic Niskin bottles mounted on a rosette equipped with an SBE 19plus CTD probe. Sulfate concentrations were determined in samples from station Ash-25.

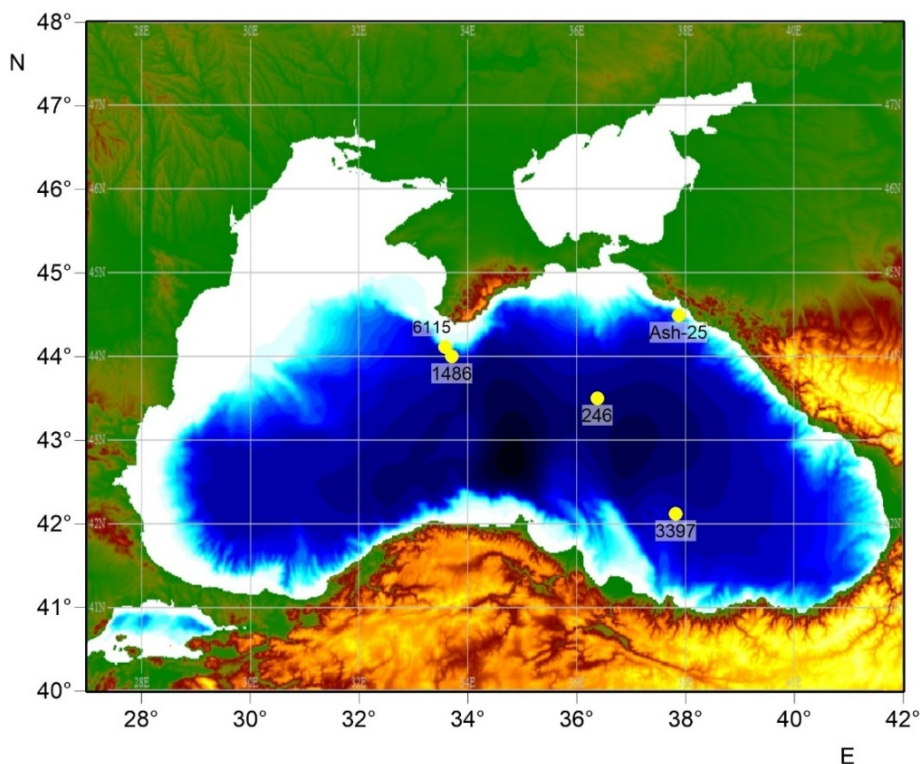


Fig. 1. Locations of the stations in the Black Sea

In the central part of the sea, the chlorinity and sulfate concentration were obtained at station 246 for 24 samples from the surface to a depth of 1972 m (Fig. 1). Sampling was carried out on May 6–7, 2021 during the expedition of R/V *Professor Vodyanitsky* with a cassette of 12 Niskin bottles equipped with SBE 19plus CTD probe.

In water samples taken in the R/V *Professor Vodyanitsky* expedition immediately on board the ship (and in the Black Sea 2021 expedition after returning to the shore) in the evening of the same day, the oxygen concentration was measured by the Winkler method [12] and hydrogen sulfide – by the method of photometry with methylene blue without preliminary dilution of samples to a concentration of 25 μM H_2S and with preliminary dilution above these

concentrations of hydrogen sulfide [13]. Samples for the oxygen and hydrogen sulfide determination were recorded immediately after they were taken from the bottle. For the gravimetric determination of sulfate, two samples were taken into pre-weighed polypropylene test tubes 50 ml in volume, where 3 ml of a zinc acetate (5%) solution of a known mass was added. Samples from the anaerobic zone were taken into test tubes with zinc acetate. Without zinc acetate addition, the water samples without H₂S were taken. The tubes were capped, frozen at -18 °C, and stored in this form until analysis. Chlorinity in the Black Sea 2021 expedition was measured immediately after the vessel returned to the Southern Branch of the IO RAS for the next 1–2 days. During the R/V *Professor Vodyanitsky* expedition, 125 ml samples for the chlorinity determination were stored in narrow-necked polypropylene jars with lids fixed with parafilm at +4 °C and analyzed within three weeks after sampling.

The method of gravimetric determination of sulfate concentration in the Black Sea water is briefly described in [11]. The gravimetric determination of sulfate is the most accurate method used for sea water [1]. A weighed aliquot of seawater (20 g) from the anaerobic zone with pre-weighed (3 ml) 5% zinc acetate added prior to collection is filtered through a 'blue tape' filter paper. Samples without zinc acetate (20 g) are taken for the sulfate determination without pre-filtering. After filtration, the filter is washed with bidistilled water and the sample volume is adjusted to 100 ml. For a sample from one test tube, two parallel determinations are carried out. The method reproducibility was evaluated based on the standard deviation determination equation $SD = (\sum (x_1 - x_2)^2 / 2n)^{1/2}$, where x_1 and x_2 are the results of parallel determinations; n is the number of samples. It was 0.017 mmol/kg or less than 0.10 rel. % for samples ($n = 23$) from station 246 and 0.024 mmol/kg or 0.17 rel. % for samples ($n = 13$) from station Ash-25. Accuracy of the determinations was assessed by using the IAPSO Seawater Standard (Practical Salinity 34.993; Batch P162). Since the IAPSO Seawater Standard is not certified for sulfate concentration, for its calculation we use chlorinity ($S/1.80655$) and an average sulfate-chlorinity ratio of 0.1400 g/g in sea water [1, 14]. The calculated value of sulfate concentration was 28.23 mkmol/kg and did not differ within 2σ from the obtained value of 28.32 ± 0.06 (σ) at $n = 6$.

Chlorinity determination was carried out according to the method [1] (high accuracy mode), modified for KEM AT-710 potentiometric titrator (Kyoto Electronics Manufacturing, Japan) with a combined silver electrode. The titrator is equipped with two 10 ml automatic burettes. The IAPSO Seawater Standard (Practical Salinity 34.993; Batch P162) was used as the reference sample. The reproducibility of the chlorinity determination was 0.011 rel. %, which is an order of magnitude better than the reproducibility of data for sulfate. Consequently, errors in the sulfate-chlorinity ratio calculation will be determined mainly by the sulfate determination errors. For water taken at station 246, the standard deviation for 23 pairs of determinations of the sulfate-chlorinity ratio was ± 0.0001 , for station Ash-25 (13 determinations) – ± 0.0002 .

Research results

Chlorinity on the continental slope was measured at two stations at the same point, but with a time difference of five days. It varied from 9.77 to 12.22 g/kg with a change in conductometric salinity from 17.72 to 22.11 PSU (Tables 1 and 2).

Table 1

Salinity and hydrochemical parameters of the water column at station Ash-23

Depth, m	Salinity	H ₂ S, μM	O ₂ , μM	Cl, g/kg
6.1	17.729	–	253	9.789
31.3	18.542	–	307	10.235
57.9	18.701	–	288	10.321
83.2	18.939	–	248	10.445
102	19.701	–	91.3	10.858
119	20.398	–	21.0	11.235
122	20.492	–	12.8	–
136	20.763	–	4.0	11.453
149	20.934	0.54	–	11.544
153	20.969	1.32	–	–
167	21.100	4.60	–	11.635
183	21.241	12.8	–	11.728
198	21.357	24.4	–	11.798
301	21.751	74.3	–	12.020
400	21.912	118	–	12.097
500	22.019	150	–	12.171
549	22.071	192	–	12.198
600	22.109	194	–	12.220

Table 2

Salinity and hydrochemical parameters of the water column at station Ash-25

Depth, m	Salinity	H ₂ S, μM	O ₂ , μM	Cl, g/kg	SO ₄ , mmol/kg	SO ₄ /Cl, g/g
4.0	17.721	–	252.0	9.773	14.45	0.1420
30.1	18.542	–	302.0	10.230	15.14	0.1421
57.6	18.681	–	292.0	10.309	15.24	0.1420
91.4	19.014	–	230.0	10.482	15.51	0.1421
111	19.759	–	82.4	10.884	16.05	0.1416
125	20.445	–	14.3	11.279	–	–
139	20.680	–	6.8	11.408	16.74	0.1410
149	20.837	0.02	–	11.491	–	–
155	20.958	1.19	–	11.576	16.82	0.1396
164	21.045	3.18	–	11.619	–	–
170	21.089	5.30	–	11.649	16.87	0.1391
183	21.229	12.50	–	11.722	17.07	0.1399
200	21.318	19.70	–	11.763	17.18	0.1403
299	21.705	67.20	–	11.992	–	–
399	21.892	121.00	–	12.091	17.43	0.1385
500	22.019	157.00	–	12.173	17.52	0.1383
551	22.065	179.00	–	12.198	17.36	0.1367
601	22.108	193.00	–	12.223	17.44	0.1371

The sulfate concentration varied at the coastal station Ash-25 from 14.45 mmol/kg at the surface to 17.44 mmol/kg at a depth of 601 m, however, the maximum sulfate was found at a depth of 500 m and was 17.52 mmol/kg (Table 2). At station 246 maximum sulfate concentrations were found in the middle part of the water column at depths of 200, 400 and 600 m (17.47 mmol/kg) (Table 3). The minimum was found on the surface (15.37 mmol/kg), at the bottom the sulfate concentration was 17.44 mmol/kg.

The dependence of sulfate concentration on chlorinity at both stations is the same. In the samples with chlorinity less than 12 g/kg (depth up to 200 m), the behavior of sulfate is conservative. Here, with a change in salinity, the processes of mixing of desalinated surface and saline deep waters dominate. Below a horizon of 200 m, the sulfate concentration does not depend on chlorinity and starts to decrease slightly towards the bottom with an increase in chlorinity (Fig. 2).

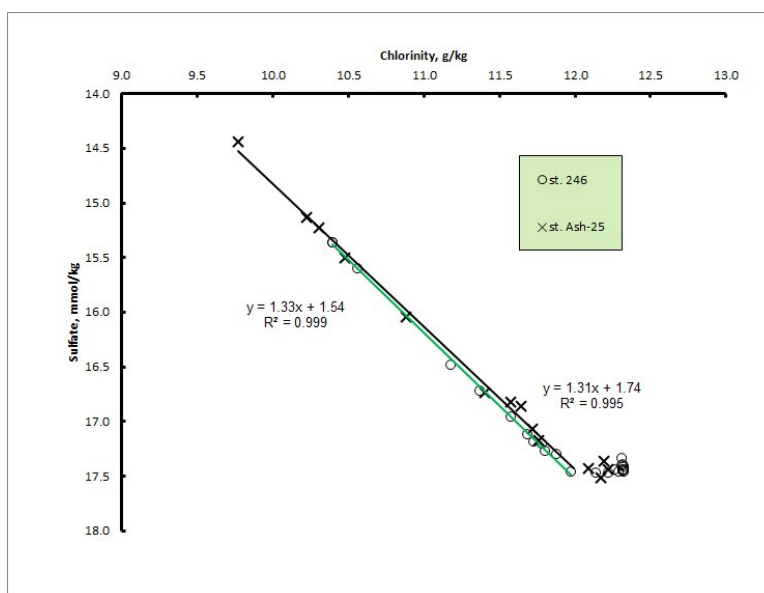


Fig. 2. Change of sulfate concentration depending on chlorinity in the Black Sea waters for stations 246 (green line) and Ash-25 (black line). Linear relationships are shown for the data with chlorinity less than 12 g/kg

The sulfate-chlorinity ratio at both stations on the sea surface is 0.1420, which is higher than in ocean water (0.1400) [1, 14]. In the deep sea (station 246), the sulfate-chlorinity ratio quite monotonously decreases down to a depth of 80 m, reaching 0.1407 (Fig. 3). At a depth of 80 m, the dissolved oxygen concentration becomes less than 3 μM , indicating suboxic conditions (Table 3). The lower boundary of the suboxic zone is above the 100 m horizon, since the concentration of hydrogen sulfide at this depth reaches 8.7 μM . The sulfate-chlorinity ratio noticeably changes in the depth interval of 80–200 m, forming minima and maxima (Fig. 3), which cannot be explained only by analysis errors. Although these deviations from linearity in the sulfate distribution relative to chlorinity are quite

small, they are still higher than $2\sigma = 0.0002$. Below the 80–200 m layer, the sulfate-chlorinity ratio decreases monotonically to a depth of 1200 m, reaching a minimum value for the station of 0.1353. Below 1200 m, the SO_4/Cl value varies within a small range from 0.1356 to 0.1361. The sulfate-chlorinity ratio at the station located on the slope changes similarly down to a depth of 600 m: from 0.1420 at a depth of 5–91 m to 0.1365 at a depth of 551 m (Fig. 4). In the upper part of the anaerobic zone at a depth of 150–200 m, a local deficit of sulfate relative to chlorinity is noticeable (Fig. 4 and Table 2). The hydrogen sulfide concentration varies in the range of 1.19–19.7 μM , and the SO_4/Cl value decreases by 0.0019 (0.1410–0.1391). In the density coordinates, the minimum sulfate-chlorinity ratio coincides at both stations and is in the range of potential density 16.3–16.6 kg/m^3 .

Table 3

Salinity and hydrochemical parameters of the water column at station 246

Depth, m	Salinity	H_2S , μM	O_2 , μM	Cl, g/kg	SO_4 , mmol/kg	SO_4/Cl , g/g
5.2	18.789	–	314	10.396	15.37	0.1420
15.2	18.803	–	305	10.397	15.37	0.1420
30.1	18.858	–	271	10.563	15.60	0.1419
45.1	20.059	–	56.0	11.184	16.48	0.1416
60.1	20.531	–	7.6	11.373	16.72	0.1412
80.1	20.905	–	< 3	11.579	16.96	0.1407
100	21.143	8.7	–	11.687	17.12	0.1407
110	21.240	13.8	–	11.730	17.19	0.1408
120	21.312	18.0	–	11.782	17.20	0.1403
130	21.369	21.3	–	11.802	17.27	0.1406
150	21.484	34.2	–	11.878	17.30	0.1400
200	21.659	54.5	–	11.973	17.47	0.1401
400	21.990	141	–	12.138	17.47	0.1383
600	22.141	216	–	12.224	17.47	0.1373
800	22.240	269	–	12.264	17.45	0.1367
1000	22.285	308	–	12.290	17.46	0.1365
1100	22.299	324	–	12.309	17.40	0.1358
1201	22.308	326	–	12.313	17.34	0.1353
1400	22.320	343	–	12.319	17.45	0.1361
1500	22.323	366	–	12.325	17.46	0.1361
1700	22.329	357	–	12.321	17.40	0.1356
1800	22.331	–	–	12.328	17.41	0.1357
1900	22.331	375	–	12.318	17.44	0.1360
1972	22.332	368	–	12.324	17.44	0.1359

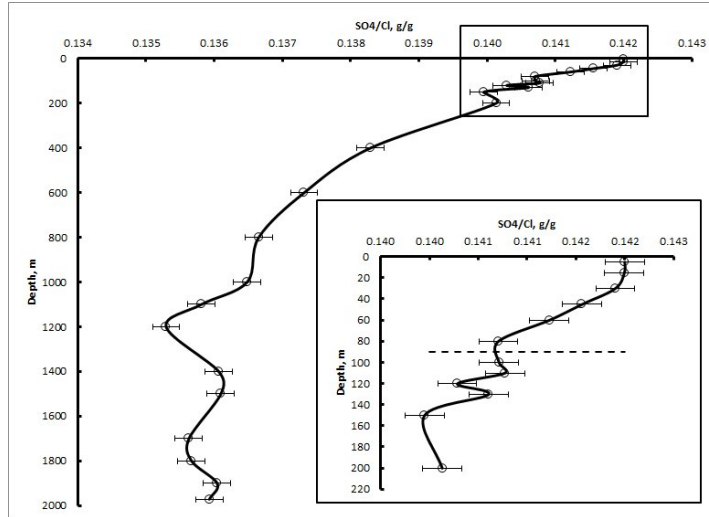


Fig. 3. Change in the sulfate-chlorinity ratio at station 246. The confidence interval is 2σ . The dotted line shows the upper limit of the anaerobic zone

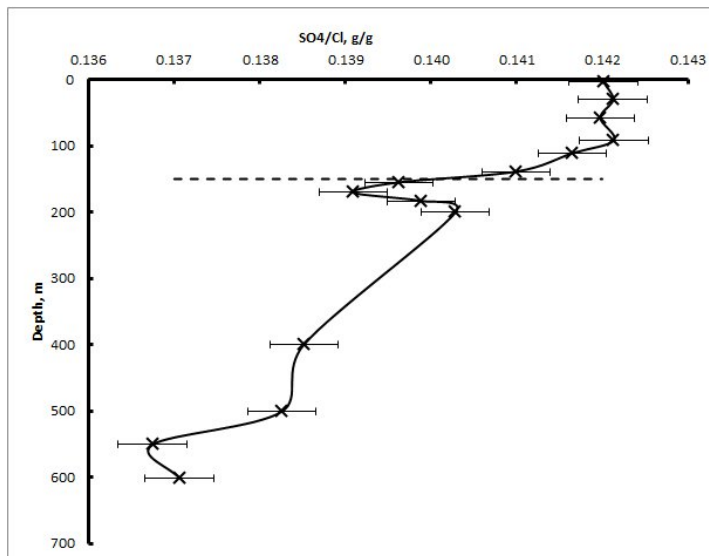


Fig. 4. Changes in sulfate-chlorinity ratio at station Ash-25. The confidence interval is 2σ . The dotted line shows the upper limit of the anaerobic zone

Discussion of the results

Two areas can be distinguished in the change in the sulfate concentration depending on the chlorinity: a linear dependence from the surface with a chlorinity of ~ 10 g/kg to depths where the chlorinity reaches 12 g/kg. When it is above 12 g/kg, the sulfate concentration does not depend on the chlorinity and decreases with depth. Based on the sulfur isotopic composition of sulfate, the reason for the decrease is the processes of sulfate reduction [9, 10]. The linear dependence of

sulfate on chlorinity determines its conservative behavior. Although a different number of samples were used for each station, the linear change in sulfate concentration (mmol/kg) depending on chlorinity in the deep sea is expressed by the following equation

$$\text{SO}_4 = 1.33(\pm 0.02) \text{ Cl} + 1.54(\pm 0.18), R^2 = 0.999 \text{ for } n = 12,$$

where Cl is chlorinity, g/kg.

For 10 samples from station *Ash-25*, this equation is as follows

$$\text{SO}_4 = 1.31(\pm 0.03) \text{ Cl} + 1.74(\pm 0.35), R^2 = 0.995.$$

For both equations, the standard deviations of the corresponding coefficients are given in parentheses. A comparison of the equations shows that, taking into account the deviations above, they do not differ.

According to our studies and the data of [6], the chlorinity changes linearly over the entire range of conductometric salinity in the Black Sea. However, the chlorine coefficient for sea water differs from the accepted value for the ocean of 1.80655. Our data shows that the chlorine coefficient in the Black Sea is 1.812 (the average for two stations *Ash-23* and *Ash-25* with high correlation coefficients was taken), which is close to the data of [6] (1.813). The method for determining chlorinity and the gravimetric method for determining sulfate have not changed significantly over decades [1]. Using data on chlorinity and salinity published in works over the past 70 years, the variations in salinity and sulfate-chlorinity ratio of the Black Sea over time to find out their change and compare it with our modern data will be analyzed.

The work ¹ presents data on sulfate and sulfate-chlorinity ratio, obtained by the authors in 1952 and 1953. They indicate an average relative standard deviation of sulfate determinations of 0.16% for 78 samples in 1952 and 0.12% for 58 samples in 1953. Our sulfate determination precision is close to that of the 1950s data. We recalculated the data on chlorinity based on the sulfate concentration and the given sulfate-chlorinity ratio (Table 4). The results of work ¹ are averaged over depths, which worsens their quality mainly in the upper part of the water column due to the convexity of isohalines to the surface in the central part of the sea. The data of 1952 show that the sulfate-chlorinity ratio on the sea surface reaches 0.1416–0.1418 (Table 4), coinciding with our data. The maximum values of the sulfate-chlorinity ratio in 1953 were also found on the sea surface, but they are lower and start from 0.1410. The minimum values of the sulfate-chlorinity ratio are at a depth of 1750 m and are 0.1363 and 0.1368, respectively, in 1952 and 1953. The maximum sulfate concentration found at the 1250 m horizon is 17.70 mmol/kg, which is significantly higher than our data (17.47 mmol/kg). However, according to 1953 data, the sulfate concentration did not exceed 17.56 mmol/kg (depth of 1500 m).

In 1974, a work containing published data on chlorinity and sulfate concentrations at station 1486 was issued [6] (see Fig. 1). The samples were taken

¹ Skopintsev, B.A. and Gubin, F.A., 1955. [Some Results of Hydrochemical Investigations in the Black Sea in 1952-1953]. In: *Trudy Morskogo Gidrofizicheskogo Instituta AN SSSR* [Proceedings of the Marine Hydrophysical Institute of AS USSR]. Moscow: AS USSR Publ. Vol. 5, pp. 71-98 (in Russian).

in 1969. Chlorinity was obtained by potentiometric titration, and sulfates were obtained gravimetrically as BaSO₄ with a reproducibility of 0.16% [6]. Chlorinity varied from 9.94 to 12.345 g/kg, the maximum concentration of sulfates, 17.46 mmol/kg, was found at the horizon of 1000 m. The sulfate-chlorinity ratio in the surface water layer to a depth of 100 m varied within 0.1417–0.1422 g/g, the minimum concentration of sulfates relative to chlorinity, 0.1340 g/g, was found at a depth of 2000 m. Nine samples with chlorinity below 12 g/kg were analyzed, the dependence of sulfate concentration (mmol/kg) on chlorinity (g/kg) is described by the following equation

$$\text{SO}_4 = 1.31 (\pm 0.04) \text{ Cl} + 1.72 (\pm 0.40),$$

with the correlation coefficient $R^2 = 0.995$. It is easy to see that the linear dependence slope completely coincides with our data (Fig. 2).

Table 4

Average sulfate concentration and sulfate-chlorinity ratio in the Black Sea waters in 1952 and 1953 according to the data ¹

Depth, m	Year of observation					
	1952			1953		
	SO ₄ /Cl, g/g	SO ₄ , mmol/kg	Cl, g/kg	SO ₄ /Cl, g/g	SO ₄ , mmol/kg	Cl, g/kg
0	0.1418	14.88	10.080	0.1410	14.82	10.097
10	–	14.98	–	–	–	–
15	–	14.97	–	–	–	–
25	0.1416	14.82	10.056	0.1408	14.86	10.138
50	0.1414	15.01	10.200	–	14.91	–
75	–	15.21	–	0.1401	15.67	10.742
100	0.1406	16.10	11.001	0.1402	16.23	11.123
125	–	16.35	–	–	–	–
150	0.1407	16.90	11.541	0.1400	16.92	11.611
200	–	17.27	–	0.1400	17.19	11.792
250	–	17.30	–	–	–	–
300	0.1395	17.45	12.016	0.1392	17.34	11.967
500	0.1386	17.54	12.156	0.1378	17.49	12.193
750	0.1385	17.66	12.249	0.1369	17.49	12.272
1000	0.1377	17.68	12.335	0.1366	17.51	12.316
1250	0.1376	17.70	12.358	0.1366	17.51	12.316
1500	0.1367	17.60	12.365	0.1372	17.56	12.298
1750	0.1363	17.55	12.367	0.1368	17.51	12.297
2000	–	–	–	–	17.48	–

The works [2, 7] present the average data on the concentration of sulfates and the sulfate-chlorinity ratio in the Black Sea water obtained for the 1985–1989 period. Unfortunately, this data has been obtained starting from 100 m depth. This makes it impossible to compare it with the data from the upper part of the water column. The average sulfate-chlorinity ratio varies from 0.1409 g/g at a depth of 100 m to 0.1369 g/g at a depth of 2000 m. These results are close to ours and previously obtained data. However, the sulfate concentrations given in these works at 500 m depth reach 17.50 mmol/kg and continue to increase continuously up to 2000 m horizon, reaching 17.83 mmol/kg. In none of the previously cited works, including our data, such high concentrations of sulfate in sea water were noted.

Along with sulfate, chlorinity increases and at the depth of 1500 m it reaches 12.59 g/kg. Deeper than 1250 m, chlorinity, according to B. A. Skopintsev and F. A. Gubin¹, varies within 12.32–12.37; according to [6], it is close to 12.34, according to our data it is 12.33 g/kg. As can be seen, over the past 70 years, the differences in the chlorinity of the deep Black Sea did not exceed 0.05 g/kg and are maximum for the data for 1952 and 1953¹. Therefore, most likely, the high average chlorinity in 1985–1989 reflects the presence of a systematic error in the determination. This can be verified by converting chlorinity to conductometric salinity using the chlorinity factor of 1.813 from [6] as based on a large material of 122 samples. Conversion of chlorinity to salinity (g/kg) using the formula $S = 1.813 Cl$ in the bottom convective layer at 2000 m depth for average data for 1985–1989 results in a value of 22.68, being 0.35 higher than the salinity observed on the 1988 R/V *Knorr* expedition [4]. The time of observation [4] coincides with the time of the data obtained in [2, 7].

Average sulfate concentration data in the works of the same authors are unjustifiably overestimated. Below 500 m, the sulfate concentration becomes more than 17.65 mmol/kg and continues to increase up to 17.99 mmol/kg at the 1,500 m horizon. The maximum sulfate concentration was found in 1952¹ and amounted to 17.70 mmol/kg at the 1250 m horizon (Table 4). However, detailed studies presented in the same works [2, 7] at station 3397 (sampling location – slope, sampling time – May 1988) and station 6155 (November 1989) (see Fig. 1, Tables 5 and 6) show that the sulfate concentration increases in proportion to the chlorinity in the depth interval of 100–250 m (up to a chlorinity value of 12 g/kg). Without anomalous sulfate concentrations, found just below the upper boundary of the anoxic zone at station 3397 (sample depth of 150–170 m and 350 m), the equation has the following form

$$SO_4 = 1.30(\pm 0.03) Cl + 1.82(\pm 0.39) \text{ for } n = 13,$$

for station 6155 –

$$SO_4 = 1.36(\pm 0.07) Cl + 1.01(\pm 0.83) \text{ for } n = 9.$$

That is, within the standard deviation, the slope of these straight lines is the same for both stations and does not differ significantly from the data of [6] and our data (see Fig. 2). This is clearly seen in Fig. 5, when the data on chlorinity and

¹ Skopintsev, B.A. and Gubin, F.A., 1955. [Some Results of Hydrochemical Investigations in the Black Sea in 1952-1953]. In: *Trudy Morskogo Gidrofizicheskogo Instituta AN SSSR* [Proceedings of the Marine Hydrophysical Institute of AS USSR]. Moscow: AS USSR Publ. Vol. 5, pp. 71-98 (in Russian).

sulfate concentrations for different years are plotted along with a linear relationship between chlorinity and sulfate for a deep-water station 246. Practically all previously obtained results below chlorinity of 12 g/kg lie along a straight line, with the exception of separate depths of station 3397.

Table 5

Sulfate concentration and sulfate-chlorinity ratio in the Black Sea waters at station 3397 according to the data in [2, 7]

Depth, m	SO ₄ , mmol/kg	Cl, g/kg	SO ₄ /Cl, g/g	H ₂ S, μM
100	16.18	11.04	0.1408	–
110	16.22	11.12	0.1401	–
120	16.42	11.23	0.1405	–
125	16.55	11.32	0.1404	–
130	16.62	11.40	0.1401	–
135	16.68	11.45	0.1399	–
140	16.85	11.50	0.1407	0.9
145	16.83	11.54	0.1401	2.7
150	16.77	11.56	0.1393	4.5
155	16.76	11.60	0.1388	7.6
160	16.70	11.62	0.1380	10.7
170	16.82	11.67	0.1385	10.7
180	17.14	11.75	0.1401	17.9
200	17.21	11.81	0.1400	25.4
250	17.24	11.90	0.1392	46.4
300	17.44	12.01	0.1395	71.0
350	17.26	12.08	0.1373	107.0
400	17.52	12.11	0.1390	120.0

Table 6

Sulfate concentration and sulfate-chlorinity ratio in the Black Sea waters at station 6155 according to the data in [2, 7]

Depth, m	SO ₄ , mmol/kg	Cl, g/kg	SO ₄ /Cl, g/g	H ₂ S, μM
100	16.15	11.09	0.1399	–
110	16.24	11.22	0.1390	–
130	16.64	11.48	0.1393	–
140	16.83	11.57	0.1397	2.2
150	16.91	11.66	0.1393	8.0
160	17.01	11.71	0.1396	15.2
180	17.00	11.81	0.1383	25.0
220	17.29	11.90	0.1396	39.7
250	17.33	12.00	0.1387	57.1
280	17.31	12.03	0.1383	74.6
300	17.26	12.05	0.1376	90.6
400	17.46	12.15	0.1380	122.0

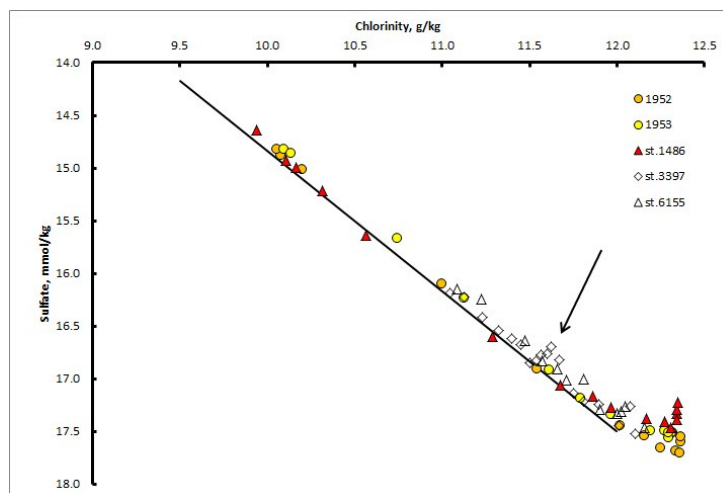


Fig. 5. Change of sulfate concentration depending on chlorinity in the Black Sea waters according to the data obtained in 1952 and 1953 ¹, 1969 (station 1486 [6]) and in 1985–1989 (stations 3397, 6155 [2, 7]). The line is the dependence of sulfate concentration on chlorinity according to our data for station 246; the arrow is the anomalously low values of sulfate concentration at station 3397

Abnormally low sulfate concentrations relative to chlorinity in the region of their linear dependence were obtained at station 3397 at hydrogen sulfide concentrations from 4.5 to 10.7 μM (Table 5 and Fig. 5) [2, 7]. The data for four depths in the depth interval of 150–170 m turned out to be lower than calculated, based on the linear relationship between chlorinity and sulfate concentration. Sulfate deficiency relative to salinity was also presented in [11]. It was identified in the upper part of the anoxic zone (potential density 16.3–16.6). However, as shown by repeated two measurements a few days later at the same station, this deficiency of sulfate lasted less than two days. Our data in this work at stations on the slope and in the central part of the sea also demonstrate an increased variability of the sulfate-chlorinity ratio in the area of occurrence of hydrogen sulfide and down to a depth of ~ 200 m (Fig. 3 and 4). These SO_4/Cl variations in the water of the upper part of the anoxic zone coincide in potential density with the maximum mass of bacterioplankton, the rate of CO_2 fixation, and the sulfate reduction rate [15]. Here, a local maximum of suspended organic matter is often present [16]. Sulfate deficiency relative to chlorinity may be the result of sulfate reduction.

The only source of salt in the Black Sea is the lower Bosphorus current. The Black Sea water balance is determined by the sum of the annual inflow of the lower Bosphorus current, river runoff and meteoric waters, the expenditure part of the balance consists of evaporation and outflow of waters with the upper Bosphorus current into the Sea of Marmara. The average volume of the lower Bosphorus current with a water salinity of 35–37 is twice lower than the volume of the upper Bosphorus current with a salinity of ~ 17 [5, 17]. Despite noticeable

¹ Skopintsev, B.A. and Gubin, F.A., 1955. [Some Results of Hydrochemical Investigations in the Black Sea in 1952-1953]. In: *Trudy Morskogo Gidrofizicheskogo Instituta AN SSSR* [Proceedings of the Marine Hydrophysical Institute of AS USSR]. Moscow: AS USSR Publ. Vol. 5, pp. 71-98 (in Russian).

variations in climatic conditions documented in [3] for 1923–1985, affecting river flow, precipitation and evaporation, the ratio of chlorinity to salinity (1.813) has not changed for 90 years, based on the data of 1931, which are mentioned by S. V. Bruevich¹. Sulfate-chlorinity ratio in the Black Sea water according to the data of 1952–1953, 1969, 1985–1989 decreased with the depth from 0.142 to 0.136 g/g and has also been stable for the last 70 years. The tangent of the linear dependence slope of sulfate concentration on chlorinity is close to 1.33 (see Fig. 2) and is typical for a conservative distribution of sulfate to a depth where chlorinity reaches 12 g/kg. The sulfate deficit relative to chlorinity, which increases in bottom waters, is not a consequence of an increase in the sulfate reduction rate, but is due to a low rate of bottom water renewal. The renewal of the bottom waters can occur only with the involvement of denser (more saline) waters of the lower Bosphorus current. This is well demonstrated by the mixing model of the waters of the cold intermediate layer, the bottom layer, and the Mediterranean Sea waters modified on the shelf [10]. The balance model based on the sulfur isotopic composition of sulfate, its concentration and salinity show that the proportion of Mediterranean waters rapidly decreases with depth to 11% at 1000 m depth [10]. The low proportion of Mediterranean waters with a sulfate-chlorinity ratio close to the oceanic one apparently does not allow to compensate for the sulfate deficit resulting from its reduction to hydrogen sulfide.

Sulfate-chlorinity ratio variations in the area below the appearance of hydrogen sulfide in water with a potential density of 16.3–16.6 kg/m³ are associated with sulfate reduction processes in the upper part of the anaerobic zone. But the formation of an unstable minimum of the sulfate-chlorinity ratio in this area, obviously, is strongly influenced by the dynamics of water masses and the hydrogen sulfide oxidation, as an additional source of sulfate.

Conclusion

A study of the sulfate-chlorinity ratio at stations on the continental slope and in the central part of the sea showed no significant differences in the behavior of sulfate and chlorinity concentrations. Up to a chlorinity of 12 g/kg, the sulfate distribution relative to chlorinity has a conservative character, which has not changed over 70 years of observations. The conservatism of the change in sulfate concentration relative to chlorinity is broken in the suboxic layer and in the upper part of the anoxic column in the range of potential density of 16.3–16.6, sometimes demonstrating sulfate deficit, which coincides with an increase in the bacterioplankton mass and the sulfate reduction rate. Below the chlorinity value of 12 g/kg in the Black Sea water, the sulfate concentration does not depend on chlorinity, and as chlorinity increases towards the bottom, the sulfate concentration decrease is observed. The reason for the decrease in the sulfate concentration in this area is the sulfate reduction processes, as a result of which the sulfur isotopic composition of sulfate changes from +21 on the sea surface to +23 ‰. The sulfate-chlorinity ratio decreases in the Black Sea water from 0.1420 on the surface to 0.134–0.136 g/g at the sea bottom. Comparison of data on chlorinity and sulfate concentration for the past 70 years shows that, within the accuracy of the analyses carried out, chlorinity and sulfate concentration remain constant, reflecting the Black Sea system steady state over this period.

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Lyubov' S. Semilova – carrying out the chlorinity and sulfate determinations, collecting the samples, reviewing and editing the original draft.

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