Characteristics of State and Evolution of the Black Sea Hydrochemical Structure

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Abstract

Purpose. The purpose of the study is to analyze the features of spatial-temporal and vertical distribution of oxygen, hydrogen sulfide and main nutrients (phosphates, nitrates, ammonium and silica acid), as well as the characteristics of carbonate system in the Black Sea in the modern period.

Methods and Results. The data used in the study were obtained by the scientists of Marine Hydrophysical Institute in the scientific cruises in the Black Sea in 2013–2021 within the economic zone of Russia. During these cruises, more than 200 deep-sea stations were carried out, samples were taken using a cassette of 12 bathometers of the Sea-Bird 911 plus CTD Seabird-Electronics INC device at certain isopycnic surfaces. At the coastal shallow-water stations, samples were taken from the surface and near-bottom horizons. Precipitations were sampled by automatic precipitation collectors at the meteorological stations located on Pavlovsky Cape in Sevastopol and at the Black Sea hydrophysical subsatellite polygon (the Southern coast of Crimea).

Conclusions. The location of upper boundary of the suboxic zone varies from $\sigma_t = 15.7$ kg/m³ to $\sigma_t = 15.9$ kg/m³, that in the depth scale corresponds to the interval of ~ 40 m. The vertical distribution of hydrogen sulfide is more of isopycnic character, the boundary of isosulfide 3 µM appearing is located within $\sigma_t = 16.10–16.15$ kg/m³. On the vertical profile of nitrates, their maximum concentration not exceeding 4 µM, is observed within the range $\sigma_t = 15.2–15.5$ kg/m³. It is shown that the content of oxidized nitrogen forms has almost returned to the pre-eutrophication level. The concentration of ammonium ions in the aerobic and suboxic zones predominantly does not exceeds 0.5 µM, the ammonium concentration starts to increase at the depth of isopycne $\sigma_t = 16.10–16.15$ kg/m³, at which hydrogen sulfide appears. The maximum concentrations of ammonium ions (96 ± 5 µM) were noted at the depth 1800 m and below that corresponded to the earlier obtained data. The phosphates vertical distribution is characterized by their minimum (< 0.5 µM) content at $\sigma_t = 15.8$ kg/m³ and by their maximum one (not more than 8 µM) at $\sigma_t = 16.2$ kg/m³. The hydrogen sulfide content at the depths exceeding 1750 m in the Black Sea is currently 383 ± 2 µM. The pH value of surface waters was 8.29–8.38 decreasing to 7.67 below ~ 50 m. Total alkalinity varied within the range 3268–3335 µM, below $\sigma_t = 16$ kg/m³ it increased sharply reaching its maximum value ~ 4364 µM in the bottom layer. The results obtained confirm the immutability of the previously established features of the vertical distribution of hydrochemical components and the ranges of their concentration variations. The spatial distribution of nutrients clearly shows a decrease in their concentrations from the coastal areas to the deep-sea ones. One of the largest external sources of nutrients the Black Sea waters is atmospheric precipitations. On the synoptic spatial-temporal scales, they can become the main source of inorganic nitrogen, phosphate and silica entering the sea surface layer.

Keywords: Black Sea, hydrogen sulfide, nutrients distribution, atmospheric deposition, hydrochemical regime

Introduction

The Black Sea is a semi-enclosed water area with the largest in the world volume of hydrogen sulfide water deeper than 130–150 m [1, 2]. Its water-salt balance is mainly determined by fresh water inflow in the northwestern part and salty water of the Mediterranean Sea through the Bosporus Strait [3, 4]. As a result, the Black Sea turns out to be permanently stratified by density. Its scale, as a rule, is used instead of the depth scale [2] when analyzing vertical distribution of hydrochemical characteristics. It offers an opportunity to take into account hydrological structure differences that arise in sea areas, in particular, in the center of cyclonic gyres and at the shelf edge. Under such an approach, it is convenient to identify individual water layers, among which the most important is the cold intermediate layer (CIL) with a core located approximately on the isopycnic surface $\sigma_t = 14.5$ kg/m^3 [4]. This layer forms as a result of density stratification when cold surface waters in winter cannot go deeper than a certain isopycnic surface of the middle part of the main pycnocline and it determines the mixing depth of the upper Black Sea layer in winter [5, 6].

The vertical distribution of almost all hydrochemical parameters is characterized by an "inflection point" in the CIL water column, where the uniform distribution of various hydrochemical components in the upper layer begins to change steadily with depth and water density. This is due to the fact that the CIL becomes the only dissolved oxygen source for the waters located below [7]. The process of photosynthesis, being another possible oxygen source, is practically absent at these depths.

Dissolved oxygen continues to be spent on the oxidation of suspended organic matter (SOM) precipitating on the top, but since only the CIL waters become the oxygen source, its content starts to monotonically decrease with depth. The oxycline formed below the CIL core gradually passes into the suboxic zone, where the oxygen concentration becomes < 10 μM, while the hydrogen sulfide content remains below its detection limit of 3 μM adopted by the back titration method [1]. There is a hydrogen sulfide zone with no oxygen below the suboxic zone and its role as an electron acceptor in the process of SOM oxidation is assumed by sulfate anions reduced to sulfides.

Such a change in redox conditions with depth or more precisely with density determines vertical distribution features of all elements of the main biogenic cycle, as well as oxygen, hydrogen sulfide, the carbonate system elements and other redox cycle components.

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[1] Bordovsky, O.K. and Ivanenkov, V.N., eds., 1978. *Methods for Hydrochemical Studies in the Ocean*. Moscow: Nauka, 271 p. (in Russian).

Nutrients content in seawater is determined by metabolic processes occurring in the water column. In addition, there are various ways for nutrients to enter aquatic ecosystems: with river waters, industrial and domestic wastewater and with atmospheric precipitation. Moreover, wet and dry deposition from the atmosphere has become an important factor influencing the state of aquatic ecosystems in many parts of the world in recent years [2] [8]. It was also reported [9–11] that the supply of substances from the atmosphere affects primary production and causes acidification of ocean waters [12, 13]. It has been established that global aeolian dissolved inorganic nitrogen (DIN) is almost equivalent to that coming from river sources and, therefore, this can have a significant impact on biogeochemical characteristics of the surface layer of the World Ocean [14].

Previous comprehensive studies of the carbonate system of the Black Sea waters [15–18], in particular, the anaerobic layer, showed a significant increase in total alkalinity at 3300–4400 μM depths at $\sigma_t > 15.9$ kg/m³. A decrease in pH, starting from 30–50 m, was also noted in these studies.

In 2013–2021, Marine Hydrophysical Institute carried out 16 complex expeditions in the Black Sea in the economic zone of the Russian Federation. Based on the data obtained, several works were published where some features of the vertical distribution of individual hydrochemical characteristics, in particular, oxygen and hydrogen sulfide [19, 20], phosphate [21] and inorganic forms of nitrogen [22] were discussed. The present paper summarizes the most important results of these studies.

Relevance of further research is determined by the fact that new data is accumulating on the hydrochemical structure of marine systems, including the Black Sea, which cannot be explained within the framework of already known concepts and the role of individual physical and biogeochemical processes in the evolution of marine ecosystems.

The present study is aimed at reviewing and summarizing modern data on the hydrochemical structure of the Black Sea waters and its evolution, primarily in the distribution of oxygen, hydrogen sulfide, nitrogen compounds, phosphorus and silicic acid, as well as on the carbonate system state (pH and total alkalinity).

Methods and materials

<u>Study area and sampling</u>. The data were obtained in 2013–2021 during expeditionary research of Marine Hydrophysical Institute, which was carried out on the R/V *Professor Vodyanitsky* and *Maria M. Merian* (November 2013). A hydrochemical sampling at deep-sea stations was carried out on isopycnic surfaces σ_t equal to 16.30; 16.20; 16.10; 16.00; 15.95; 15.90; 15.80; 15.60; 15.40; 15.20; 15.00; 14.60 kg/m³, with a cassette of 12 bathometers of a Seabird-Electronics CTD device. Fig. 1 shows the layout of the hydrochemical stations where samples for the content of oxygen, hydrogen sulfide, nutrients and carbonate system components were taken. At 8 stations, the sampling to determine the content of hydrogen sulfide, oxygen and ammonium ions was carried out by three soundings at 37 horizons: in two soundings, the samples were taken in depth from a maximum dive of 2000 m,

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[2] Krutov, A., ed., 2019. *State of Environment of the Black Sea (2009-2014/5)*. Istanbul, Turkey: Commission on the Protection of the Black Sea against Pollution (BSC), 811 p.

then after 50 m to a depth of 1800 m and then after 100 m. In the third sounding, the samples were taken along a series of isopycnals given above and from the surface.
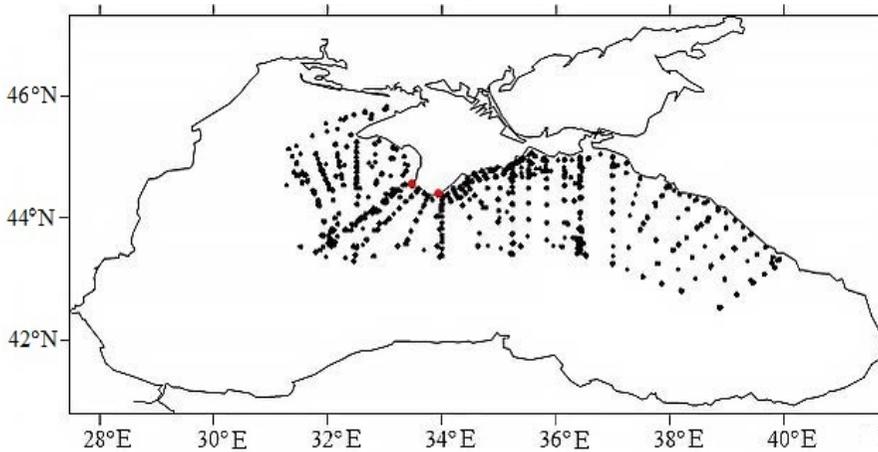
F i g. 1. Summary scheme of sampling stations during the cruises of the R/V *Professor Vodyanitsky* in 2013–2021. Red dots indicate the locations of atmospheric precipitation sampling to analyze the content of nutrients

The samples for the content of oxygen, hydrogen sulfide, ammonium ions and nitrites were analyzed on board the R/V immediately after collection. Storage and transportation of water samples for the determination of phosphate, silicic acid and the amount of nitrates and nitrites were carried out in accordance with the method and GOST 31861-2012, GOST 17.1.5.05-85. The samples passed through a 450 nm filter before analysis.

The atmospheric precipitation sampling to estimate its influence on the characteristics of the Black Sea surface layer was carried out at two points – at a weather station located on Pavlovsky Cape (Sevastopol) and at the Black Sea hydrophysical subsatellite polygon (a separate division of Marine Hydrophysical Institute in Katsiveli, the Southern coast of Crimea) (Fig. 1). The samples were taken using automatic samplers that open with the onset of precipitation and close after it finishes, as well as using permanently open samplers for each precipitation event. During sampling, meteorological parameters (relative air humidity, wind speed and direction at the beginning of precipitation, amount of precipitation) were also recorded. Atmospheric precipitation samples were frozen in plastic jars after collection. The laboratory carried out chemical analysis of samples to determine the content of inorganic nitrogen, phosphate and silicic acid using standard methods.

<u>Chemical analysis methods</u>. The oxygen content was determined by the Winkler method modified in terms of sampling with low oxygen content according to [23], the hydrogen sulfide concentration was determined by the iodometric method, taking iodine consumption at the $\sigma_t = 15.8$ kg/m^3 as zero in accordance with the method [1]. Volumetric flasks for fixing hydrogen sulfide and oxygen bottles with narrow necks were purged with argon 15 min before sampling.

The Bendschneider and Robinson method [3] was used to determine the concentration of nitrites; a modified Sagi- Solórzano method for sea water [24] was used to determine ammonium ions. The sensitivity of this method increases to 0.05 µM when using nitroprusside as a catalyst. Due to the high concentration of ammonium ions, the samples from the 500 m horizon and deeper were diluted 10 times with water taken at the same station at the $\sigma_t = 15.5$ kg/m^3 (where the absence of ammonium ions was noted).

The content of phosphate and silicic acid was determined photometrically according to [25]. The minimum detectable concentration of phosphate in accordance with the method is 0.05 µM, silicic acid – 0.1 µM.

The nitrite and nitrate sum content was determined by the spectrophotometric method according to RD 52.10.745-2020 on a Scalar San++ flow autoanalyzer by reducing nitrates to nitrites using copper-bonded cadmium. With a minimum detectable concentration of nitrates of 0.36 µM, the method error is ±0.20 µM (RD 52.10.243-293).

The pH value was measured using I-160 and I-160MP ionometers using buffer NB [4] scale solutions, total alkalinity was measured by direct titration with a potentiometric end, titrating 50 ml of sea water with a 0.02 N solution of hydrochloric acid [1] using a high-precision Metrohm Dosimat 765 piston burette and Hanna HI-2215 pH meter to determine the end point of titration. All measurements were carried out according to the paper [5].

When constructing maps of spatial distribution of nutrients and dissolved oxygen in the surface water layer, as well as their vertical distribution in the Black Sea water column, the data obtained in the spring, summer and autumn hydrological seasons were used [26]. The Gidrolog software was implemented when constructing spatial distributions, including average distributions by season.

Results and discussion

To study the evolution of the hydrochemical structure of the Black Sea, it is advisable to consider separately the surface layer (0–5 m), characterized by the greatest spatial, seasonal and interannual variability, as well as underlying layers, where the characteristics change depending on redox conditions during the transition from aerobic to anaerobic.

Spatial distribution of hydrochemical parameters in the surface Black Sea layer.

Dissolved oxygen. In spring, the dissolved oxygen distribution is characterized by significant spatial heterogeneity (Fig. 2). As expected, its concentration reaches its maximum values in early spring. Firstly, this is the result of the higher oxygen solubility in sea water at lower temperatures. Secondly, not only the content, but also

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[3] Sapozhnikov, V.V., Agatova, A.I., Arzhanova, N.V., Mordasova, N.V., Lapina, N.M., Zubarevich, V.L., Luk'janova, O.N. and Torgunova, N.I., 2003. *Guidelines for the Chemical Analysis of Sea and Fresh Waters in Environmental Monitoring of Fishery Reservoirs and Promising World Ocean Areas*. Moscow: VNIRO, 202 p. (in Russian).

[4] Bordovskii, O.K., ed., 1992. *Modern Methods of Ocean Hydrochemical Investigations*. Moscow: IOAN, 199 p. (in Russian).

[5] Dickson, A.G. and Goyet, C., eds., 1994. *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water. Version 2*. Oak Ridge, TN: Oak Ridge National Lab. (ORNL), 198 p. doi:10.2172/10107773

the degree of water saturation with oxygen increases due to photosynthesis activation during this period, the dissolved oxygen content is maximum and the surface layer is oversaturated with it (Fig. 2, *a*). At the beginning of spring, oxygen concentration can reach 328 μM, which at surface layer temperature of ~ 9 °C corresponds to 103% saturation. In late spring, with significant heating of the surface water layer to 22–23 °C, its concentration decreases to 277 μM, while the oxygen saturation degree of the water is maximum and reaches 114%. The average oxygen concentration is 284 μM, which corresponds to 105% saturation.
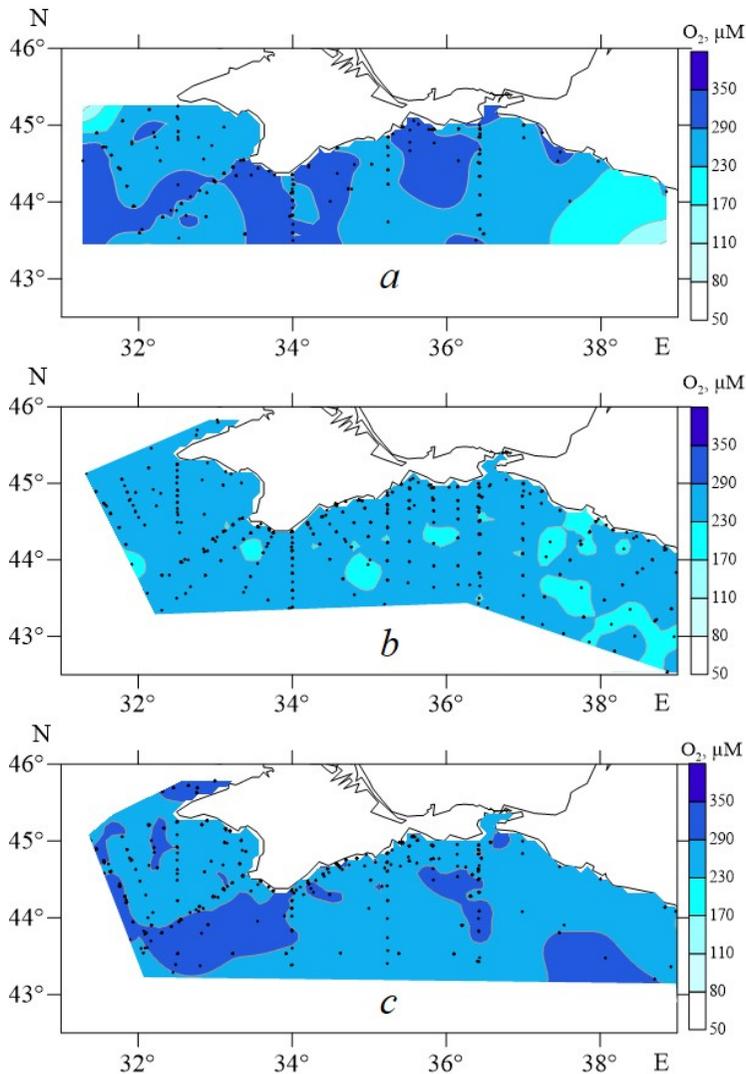
F i g. 2. Spatial variability of dissolved oxygen concentration in the Black Sea surface layer in spring (*a*), summer (*b*) and autumn (*c*)

In summer, the oxygen content is reduced to minimum values ~ 241 μM (Fig. 2, *b*) due to the warming of water to an average of 24–25 °C, reducing oxygen

solubility and intensification of oxidation processes of organic matter and leading to oxygen consumption, as well as due to water stratification, limiting the vertical flow of oxygen. The saturation of water with oxygen is close to the equilibrium state (101% saturation). Locally, zones of oxygen deficiency (< 80%) were noted in individual surveys (September 2018 and 2020).
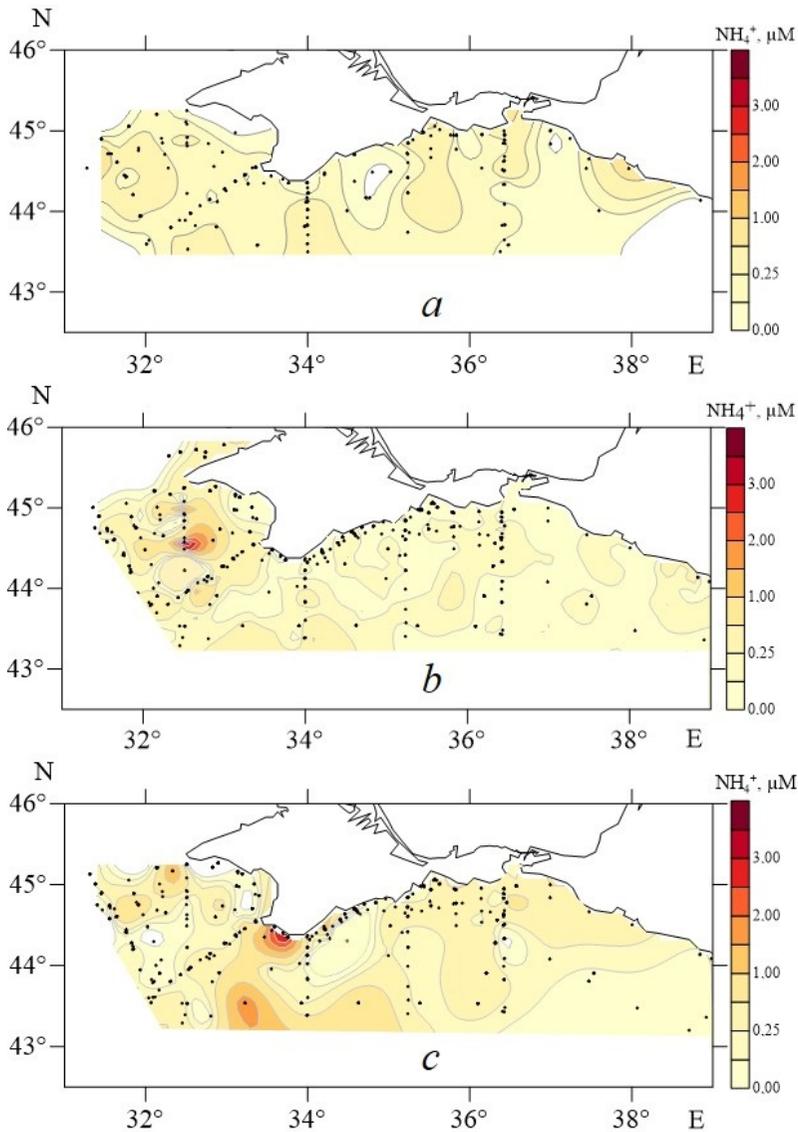
F i g. 3. Spatial variability of ammonium concentration in the Black Sea surface layer in spring (*a*), summer (*b*) and autumn (*c*)

As autumn cooling of the Black Sea waters (on average to 15–16 ºC) starts, there is an increase in the dissolved oxygen concentration to an average of 279 μM, water

saturation degree with oxygen reaches 100%. However, in the central deep-sea part its local maxima are observed (up to 105% saturation in October 2020) (Fig. 2, *c*).

On average, oxygen saturation degree of surface waters in 2013–2021 varied within 100–105%. In some cases, values could decrease to 54–70% saturation in summer.

Inorganic nitrogen forms. In spring and summer, the spatial distribution of ammonium ions was uniform with average concentrations of 0.19–0.22 μM. Local maxima of ammonium content were noted in the Sevastopol coast area in autumn (Fig. 3, *c*) and in summer – in the Sevastopol anticyclone area (Fig. 3, *b*).

The maximum content of ammonium is typical for autumn period (Fig. 3, *c*). The concentrations ranged from 0.00–3.23 μM with a mean value of 0.32 μM. This is probably due to the vertical mixing of waters and the supply of ammonium ions from underlying layers in late autumn. In addition, ammonium ions are one of the products of organic matter oxidation [22]. It is likely that by early autumn, ammonium ions accumulate in the surface layer of water as a result of organic matter oxidation in summer.

Oxidized nitrogen (the sum of nitrates and nitrites) turned out to be the only nutrient element with a relatively constant content in all seasons (Fig. 4). Just as in the dissolved oxygen distribution, the greatest spatial heterogeneity in the distribution of the sum of nitrates and nitrites was observed in spring (Fig. 4, *a*). Increased concentrations of these forms of nitrogen in spring were observed in the coastal areas of Evpatoria, Sudak and Novorossiysk, which can be explained by the influence of coastal discharge.

It is worth noting that increased concentrations of these forms of nitrogen in both spring and autumn were determined in the area of the Sevastopol anticyclone periphery [27].

Phosphate and silicic acid. The distribution of phosphate in the surface water layer in spring is relatively uniform and their average concentration does not exceed 0.1 μM (Fig. 5).

In summer, the distribution uniformity is disrupted; in the surface waters of the deep-sea part, the concentration decreases to 0.05 μM (Fig. 5, *b*), while in coastal waters (especially near the Southern coast of Crimea) the phosphate content exceeds 0.3 μM. It can be assumed that this concentration distribution is caused by the supply of phosphate from coastal sources, whose power increases during holiday season. The decrease in phosphate concentration in the deep-sea part may be due to their consumption in the photosynthesis process and the lack of supply from deeper water layers due to stable seasonal stratification.

By autumn (Fig. 5, *c*), a uniform distribution of phosphate is restored and their concentrations decrease to the spring level (< 0.1 μM).

In silicic acid distribution in spring, its clear accumulation in the deep-sea part (up to 6.5 μM) can be noted. Moreover, an unexpected result was its lower concentrations (2.5–4.5 μM) compared to the deep-water part at the confluence of rivers being the main source of silicon, which are characterized by maximum flow in spring (Fig. 6).
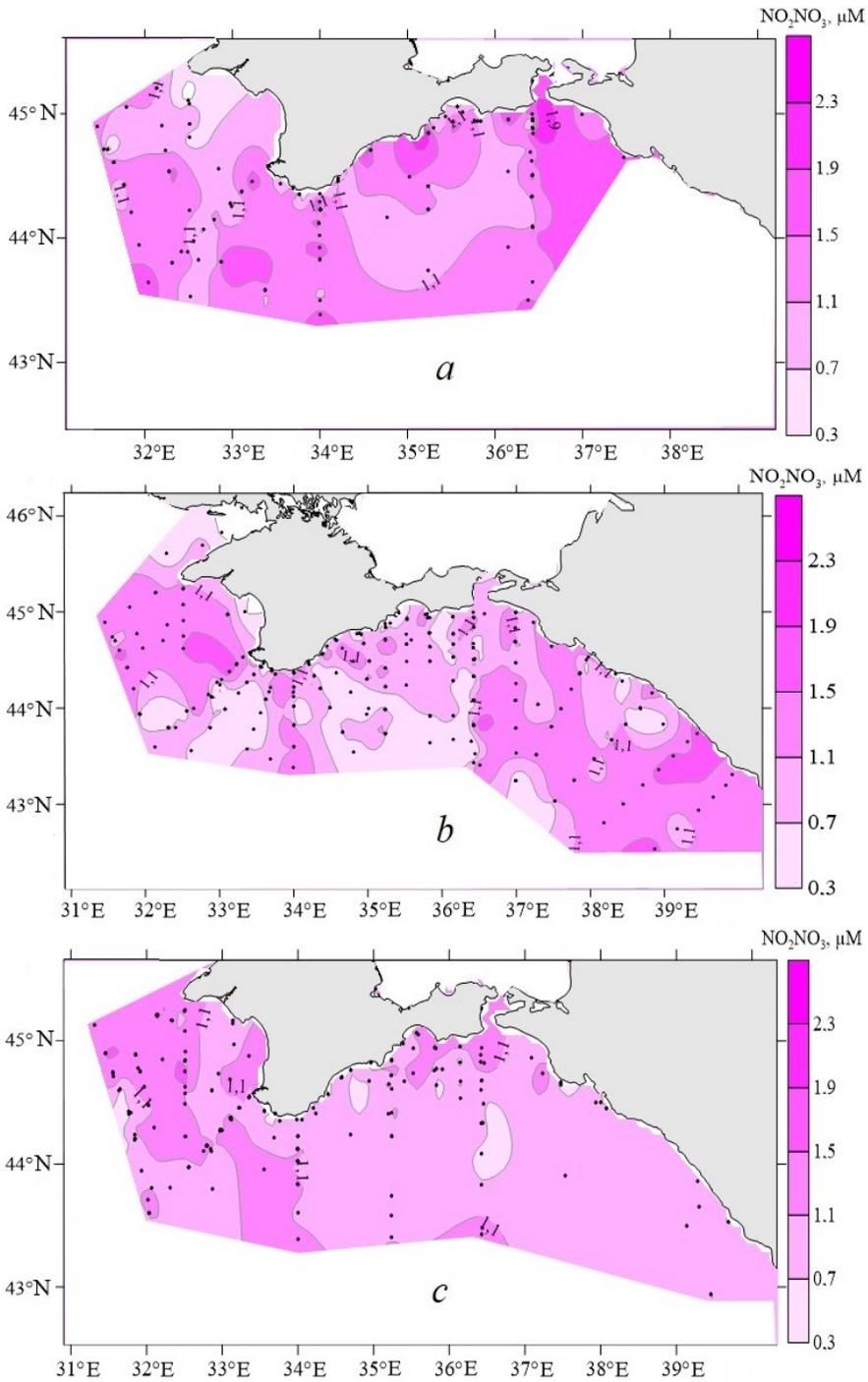
F i g. 4. Spatial variability of oxidized nitrogen concentration in the Black Sea surface layer in spring (*a*), summer (*b*) and autumn (*c*)
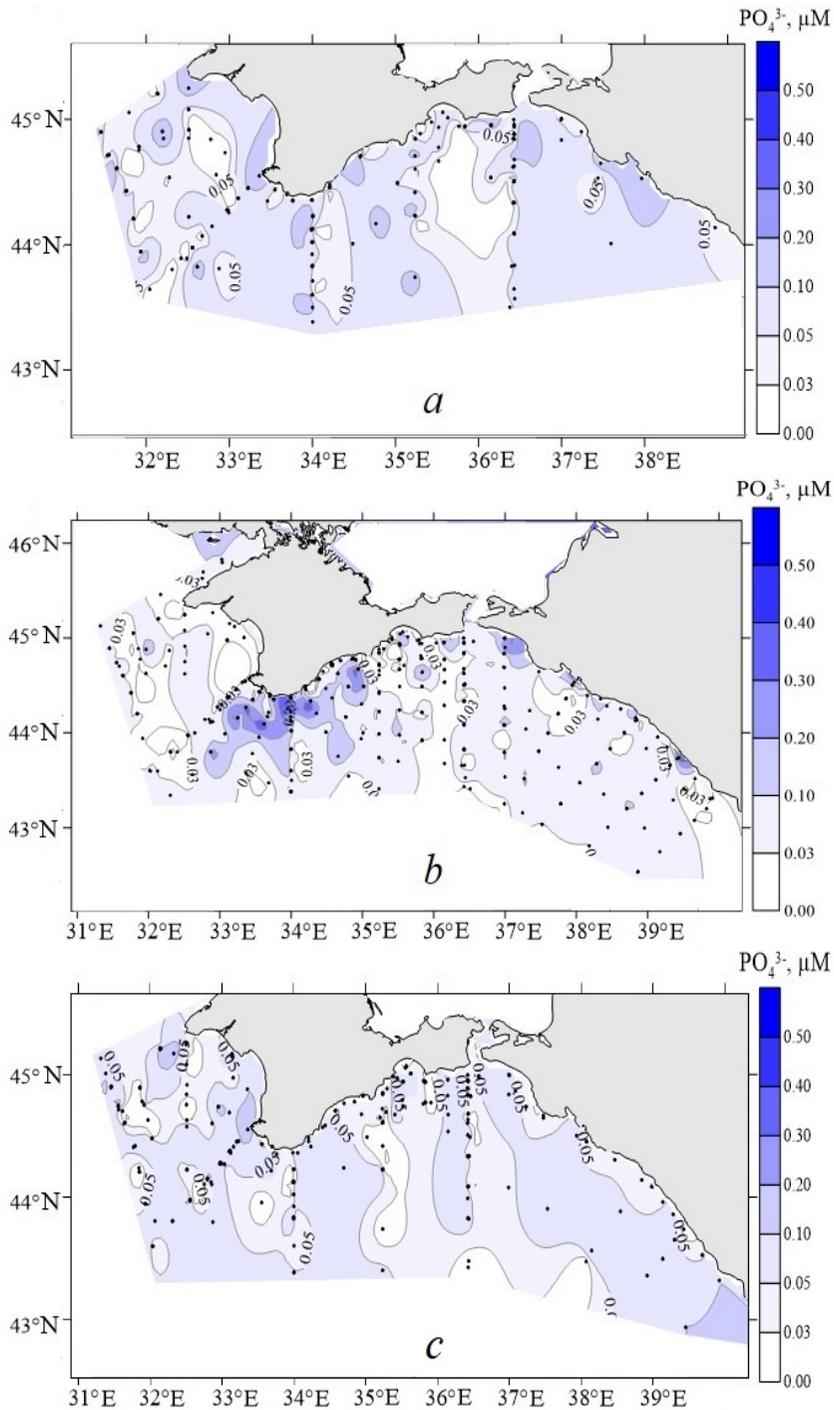
F i g. 5. Spatial variability of phosphate concentration in the Black Sea surface layer in spring (*a*), summer (*b*) and autumn (*c*)
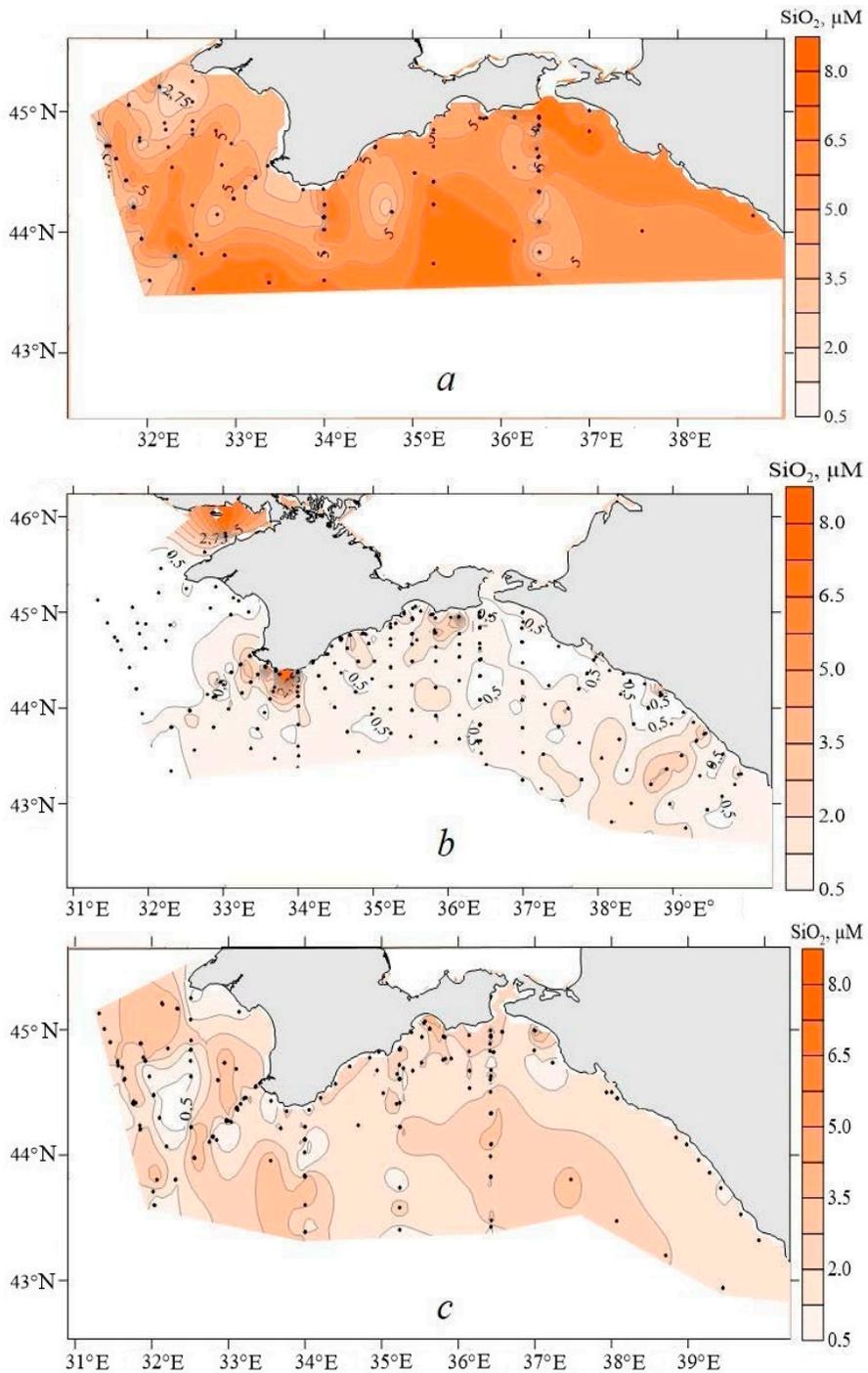
F i g. 6. Spatial variability of the silicic acid concentration in the Black Sea surface layer in spring (*a*), summer (*b*) and autumn (*c*)

The only coastal area where silicic acid concentrations, comparable to its values in the deep-sea part are observed, is the Kerch Strait area (6.5 µM). The source of silicic acid here is probably the Azov Sea waters. Therefore, the predominant factor in the spatial distribution of silicic acid is water dynamics and vertical exchange with the underlying layers where it accumulates in winter.

In summer, the average silicic acid content decreases by 3–5 times compared to winter (Fig. 6, *b*). A local maximum concentration was noted near the Katsiveli coast. Silicic acid content in the deep-sea part was minimal, 1 µM or less. In autumn, its concentration increases slightly compared to summer and reaches 1–3 µM (Fig. 6, *c*).

Contribution of atmospheric precipitation to the distribution of nutrients in the surface water layer. According to the data [6], in 2019, the annual export of inorganic nitrogen with rivers to the northwestern Black Sea was $332.5 \cdot 10^3$ t/year, phosphate – $17.25 \cdot 10^3$ t/year, silicic acid – $603.1 \cdot 10^3$ t/year. The Kamchia River, located in Bulgaria, annually supplies $\sim 3.3 \cdot 10^3$ t/year of inorganic nitrogen and $\sim 0.2 \cdot 10^3$ t/year of phosphate. Inorganic nitrogen supply with rivers in the Russian sector of the Black Sea is estimated at $0.8 \cdot 10^3$ t/year, phosphorus – at $0.08 \cdot 10^3$ t/year, inorganic nitrogen in the area of the Georgian coast – at $1.3 \cdot 10^3$ t/year; Turkish rivers annually supply $\sim 40 \cdot 10^3$ t/year of total nitrogen and $\sim 11 \cdot 10^3$ t/year of total phosphorus to the Black Sea [2].

The annual wastewater flow into the Black Sea is estimated at $6.12 \cdot 10^3$ t for inorganic nitrogen and at $2.15 \cdot 10^3$ t for inorganic phosphorus. Industrial sources of nutrients annually contribute $1.18 \cdot 10^3$ t of inorganic nitrogen and $0.25 \cdot 10^3$ t of phosphate [2]. The average input of dissolved inorganic nitrogen (the sum of nitrites, nitrates and ammonium) with precipitation in the Crimean coast area is 32.0 mM/m^2·year. Based on the obtained values, the flow of nitrogen with precipitation to the Black Sea surface (area 429,000 km^2) can reach $18.3 \cdot 10^{12}$ mM/year, or $192 \cdot 10^3$ t/year of inorganic nitrogen.

The average supply of phosphate and silicic acid with precipitation in the Crimean coast area is ~ 0.6 mM/m^2·year according to the data from two sampling points. The average annual supply of dissolved phosphorus with precipitation to the Black Sea surface can reach $0.78 \cdot 10^{12}$ mM/year, or $8 \cdot 10^3$ t/year of inorganic phosphorus. The flow of dissolved silicon with precipitation on the Black Sea surface is $0.26 \cdot 10^{12}$ mM/year, or $7 \cdot 10^3$ t/year.

The generalized values of inorganic nitrogen and phosphate that enter the Black Sea from various sources, according to the published and our data on inflow with precipitation, are given in the table.

Nutrients from various sources entering the Black Sea

Source	DIN, 10^3 t/year	P-PO_4, 10^3 t/year
River discharge	362 (64.5%)	24.0 (69.8%)
Industrial sources	1.2 (0.2%)	0.25 (0.7%)
Sewage waters	6.1 (1.1%)	2.15 (6.2%)
Atmospheric precipitation	192 (34.2%)	8.00 (23.3%)
Total	561.3 (100%)	34.4 (100%)

[6] Lazăr, L., ed., 2021. *Impact of the Rivers on the Black Sea Ecosystem*. Buchurest, Romania: Editura CD Press, 225 p.

According to the table, river discharge is the predominant source of inorganic nitrogen and phosphorus entering the Black Sea, atmospheric precipitation is the second most powerful source. However, the contribution of coastal sources, as well as river discharge, mainly affects coastal and estuarine areas. Only ~ 2.2% of the total amount of nutrients supplied with river discharge reaches the deep-water part of the sea [28]. One of the sources of nutrients in the surface layer is also the supply from deep cold waters during upwelling [29]. However, this source manifests itself mainly in summer, when stable stratification of the Black Sea waters contributes to the limited vertical exchange. We can conclude in accordance with our data that in deep-sea areas precipitation on synoptic spatial-temporal scales can be the main source of inorganic nitrogen, phosphate and silicic acid entering the surface layer.

Carbonate system. One of the main carbonate system parameters is pH and total alkalinity, which are determined as follows [30]:

$$pH = -\log a_{H^+},$$
$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [H_3SiO_4^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [OH^-],$$

where aH^+ is value of hydrogen ion activity. Seawater pH value depends on the carbon dioxide content in it and its redistribution into various forms of carbonic acid with the release or capture of hydrogen ions to achieve equilibrium [31]:

$$CO_2aq + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+.$$

Total alkalinity is determined primarily by the total content of hydrocarbonates and carbonates and, to a much lesser extent, by derivatives of boric, silicic and phosphoric acids. In the anaerobic zone, total alkalinity is also largely determined by the contribution of ammonium and hydrogen sulfide components.

Spatial variability of pH within a single expedition significantly exceeds the seasonal variability of the average values of this quantity. Its causes can be both natural factors (hydrological and hydrodynamic processes, such as mixing of the Sea of Azov and the Black Sea waters; local biological anomalies) and anthropogenic ones (terrigenous runoff, intensive shipping, industrial activity).

An intra-annual distribution of measurements in the surface water layer is shown in Fig. 7. The measurements were carried out from the second half of April until the end of December.
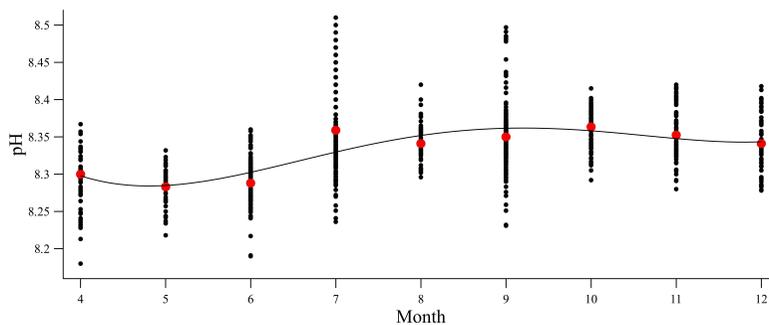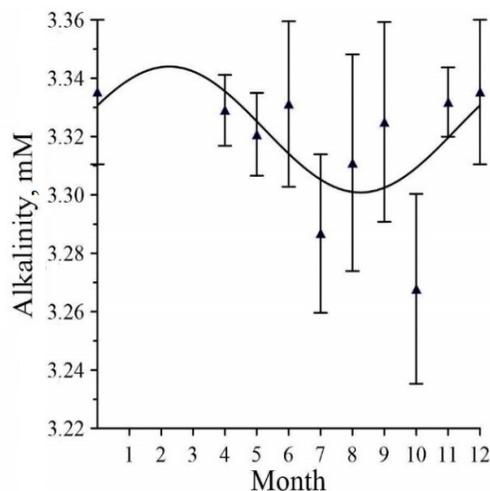

F i g. 7. Intra-annual variability of average (median) values (•) and all the measurements (•) of pH of surface waters in the northern part of the Black Sea based on the data obtained in 2013–2021

An intra-annual variation of average pH values of surface waters in the northern part of the Black Sea can be divided into six months. From July to December, pH is almost constant and varies between 8.34–8.36 units (standard deviation 0.01 pH units, which does not exceed the measurement method error and is statistically insignificant). The minimum average values are observed in spring amounting to 8.29 ± 0.01 pH units in May – June (Fig. 7). Then the pH begins to rise again, reaching the values of the second half of the year.

As for long-term variability, no statistically significant downward or upward trend was detected for the pH value of surface waters in the northern part of the Black Sea during the study period (2013–2021) and the range of spatial-temporal pH variation is 8.29–8.38.

The spatial variability of total alkalinity values within a single expedition (117th cruise of R/V *Professor Vodyanitsky*) influenced by both natural and anthropogenic factors reached 180 μM not exceeding an average of 90 μM. These values are 1.3 times (2.7 at maximum scatter) less than the variation range of seasonal median values. The main factors determining the differences in the total alkalinity spatial distribution are the influx of carbonates with river discharge in the coastal part of the area under study and the influx of the Sea of Azov waters, the alkalinity of which is one third lower than that of the Black Sea. At the same time, the waters of the Sea of Azov mixing with the Black Sea ones determine a decrease in the alkalinity of the Black Sea surface waters due to their lower density.

For average values of total alkalinity of surface waters of the northern part of the Black Sea, seasonal variability is characterized by a sinusoidal variation with minimum values (3.268–3.283 mM) in the summer-autumn period (July – early October) and with maximum values presumably in winter-spring period (Fig. 8). Moreover, the difference between the minimum and maximum average values is 66 μM, which is more than 10 times the error of the measurement method [5].


F i g. 8. Seasonal variability of the total alkalinity average (median) values of surface waters in the northern part of the Black Sea based on the data obtained in 2013–2021

In spring, alkalinity should be determined by the contribution of terrigenous runoff and river discharge, which are the main sources of hydrocarbonates and carbonates. Organic matter oxidation processes have low influence on the total alkalinity dynamics. In the summer-autumn period, it decreases as a result of calcium carbonate formation with carbon dioxide release [31]:

$$Ca_2^+ + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O.$$

Vertical distribution of hydrochemical parameters in 2013–2021

Oxygen and hydrogen sulfide. Fig. 9 presents vertical profiles of oxygen and hydrogen sulfide averaged from the natural data: in the water column relative to the density scale (Fig. 9, *a*, the solid line indicates the beginning of the oxycline, where a sharp change in the vertical gradient of oxygen concentration occurs) and in more detail – within the range of $\sigma_t = 15.5–16.3$ kg/m^3, where the upper boundaries of the suboxic zone and hydrogen sulfide occurrence are located (Fig. 9, *b*).
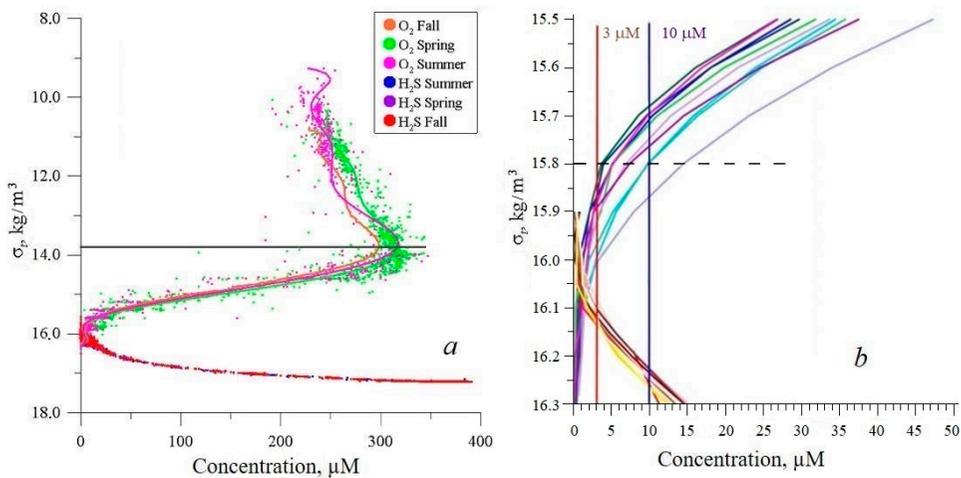
F i g. 9. Concentrations of oxygen and hydrogen sulfide throughout the whole water column (*a*) and in the range $\sigma_t = 15.5–16.3$ kg/m^3 (*b*) in different seasons

The oxycline beginning in the period under consideration was located at the isopycnaic surface ~ 13.8 kg/m^3 and was not subject to seasonal changes (Fig. 9, *a*).

The position of the suboxic zone upper boundary, determined by an oxygen concentration of 10 μM, varies from $\sigma_t = 15.7$ kg/m^3 to $\sigma_t = 15.9$ kg/m^3 (which corresponds to an interval of 40 m on the depth scale). The deepest position of the suboxic zone upper boundary, $\sigma_t \geq 15.8$ kg/m^3, was observed in November and December 2017, as well as in August 2018. It should be noted here that 2017 was characterized by an increase in oxygen saturation of the entire water column during 2009–2019 [32]. This is due to a relative decrease in temperature in 2017 and an increase in the CIL oxygen concentration compared to the previous and subsequent years [33]. Apparently, this oxygen supply ensured deepening of the suboxic zone upper boundary in November 2017.

The vertical distribution of hydrogen sulfide turned out to be more isopycnal compared to the distribution of oxygen and isosulfide 3 μM was located within the isopycnal range of 16.10–16.15 kg/m^3.

Maximum hydrogen sulfide concentrations in the Black Sea. At 8 deep-sea stations, hydrogen sulfide profiles were studied within the depth interval of 1750–2000 m. As it is known, a uniform distribution of hydrological and hydrochemical characteristics is observed in the bottom waters of the Black Sea below 1750 m due to convective mixing owing to the heat coming from the bottom surface [26]. The maximum hydrogen sulfide content and its variation trends are of greatest interest. In particular, at the end of the previous century, a significant increase in the hydrogen sulfide concentration from ~ 300 to ~ 390 μM was observed in the bottom water layer, after that its content stabilized at 378– 387 μM [2].

According to the data from 2017–2019, the hydrogen sulfide concentrations at deep-sea stations below 1750 m varied within 378–385 μM and corresponded to the interval presented above. When combining the values for all stations into one array after statistical verification [7], we found that the hydrogen sulfide content at > 1750 m depths in the Black Sea is currently 383 ± 2 μM.

Inorganic forms of nitrogen. Of all the nutrients in the Black Sea, inorganic forms of nitrogen are characterized by the greatest variety of redox forms – a transition from an oxidized state to reduced forms ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \rightarrow NH_4^+$), which is determined primarily by the content of dissolved oxygen in the water column and depends on the hydrological structure characteristics [34, 35].

In the upper productive layer, where photosynthesis occurs, the main form of nitrogen are nitrates, since ammonium formed during the SOM mineralization and the intermediate product of its oxidation, nitrites, are quickly oxidized in the presence of a sufficient amount of oxygen (a nitrification process occurs). The nitrates does not accumulate in the upper productive layer, since it is used by phytoplankton in the process of photosynthesis [32].

With depth, the amount of incoming light decreases, photosynthesis weakens and the content of dissolved oxygen decreases. However, while there is enough dissolved oxygen for nitrification, a gradual accumulation of nitrates takes place, and these nitrates do not have time to be extracted by phytoplankton. This accumulation leads to a peak in their concentration, which for the Black Sea is located where the gradient of decreasing oxygen concentration passes through a maximum, approximately at the σ_t = of 15.5 kg/m^3 [34].

Below the oxycline upper boundary, the nitrates content gradually increases compared to the layers where oxygen deficiency is absent (above σ_t = 14.0 kg/m^3) and reaches a maximum on the isopycnic surface σ_t = 15.2–15.5 kg/m^3, which is the result of the SOM aerobic destruction. After this, nitrates concentrations rapidly begin to decrease with depth – when the oxygen concentration drops below < 10 μM,

[7] Sevastyanov, B.A., 2019. *A Course of Probability Theory and Mathematical Statistics. Textbook.* Moscow-Izhevsk: Institute of Computer Research, 272 p. (in Russian).

denitrification reactions occur and result in the removal of nitrates. In addition, the amount of oxygen is no longer enough to oxidize ammonium ions coming from the underlying layers to nitrates [34–36].

During the period under review, the layer of maximum nitrates (the sum of nitrates and nitrites) in the aerobic zone was slightly lower in the cold season (November – December) than in the warm months. At the same time, the minimum content of oxidized nitrogen in the maximum layer was observed in August (Fig. 10).
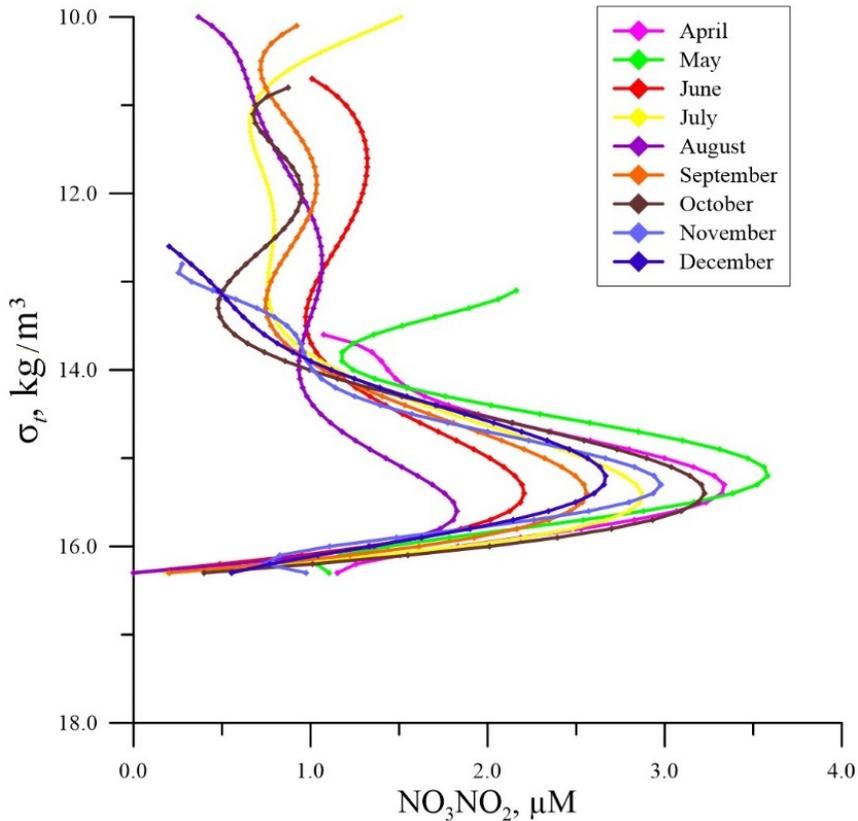
**F i g. 10.** Averaged vertical profiles of the nitrates and nitrites sum by months

The vertical distribution of oxidized nitrogen relative to the density (Fig. 11) was characterized by the maximum value of averaged concentration, which was 3.0 –3.5 μM in 2013 and 2016. The content of nitrates in the maximum layer was maximum in 2013–2017 and it was within the range of density ~ 13.5–16.2 kg/m³.

In subsequent years, the maximum concentrations of the sum of nitrates and nitrites were observed at isopycnic surfaces ~ 14.5–16.0 kg/m³ (Fig. 11, *b*) and amounted to 1.8–2.6 μM. These values correspond to pre-eutrophication indicators [4], which may indicate a decrease in anthropogenic load on the Black Sea ecosystem.
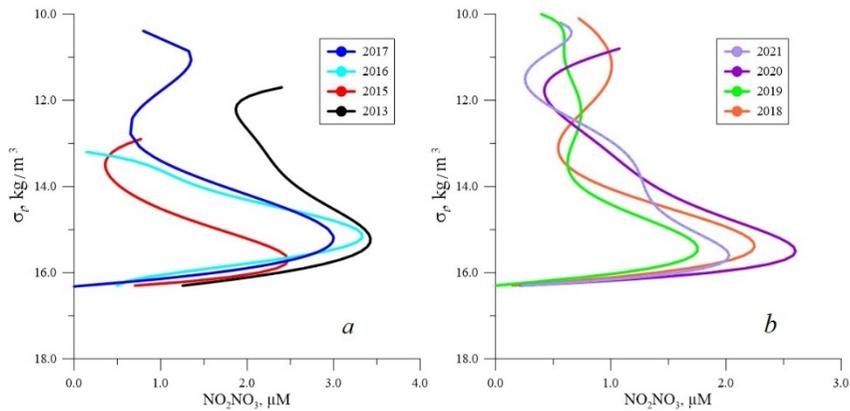
F i g. 11. Averaged vertical profiles of the nitrates and nitrites sum in 2013–2017 (*a*) and 2018–2021 (*b*)

The oxidized nitrogen concentration decreases to almost zero at a depth corresponding to a density value of ~16.2 kg/m^3. At the same depth, the concentration of ammonium begins to monotonically increase (Fig. 12) down to σ_t = 17.0 kg/m^3. In the aerobic zone, ammonium ions are oxidized to nitrates/nitrites due to the presence of oxygen and this determines their relatively low concentrations in this layer of water: they rarely exceed 0.5 μM and, on average, are ~ 0.22 μM. As the oxygen content decreases (in σ_t = 15.9–16.1 kg/m^3 layer), the concentration of ammonium ions is determined by denitrification, which leads to a clear and rapid increase in ammonium content below the boundary of hydrogen sulfide occurrence at σ_t = 16.1 kg/m^3 (Fig. 12, *b*).
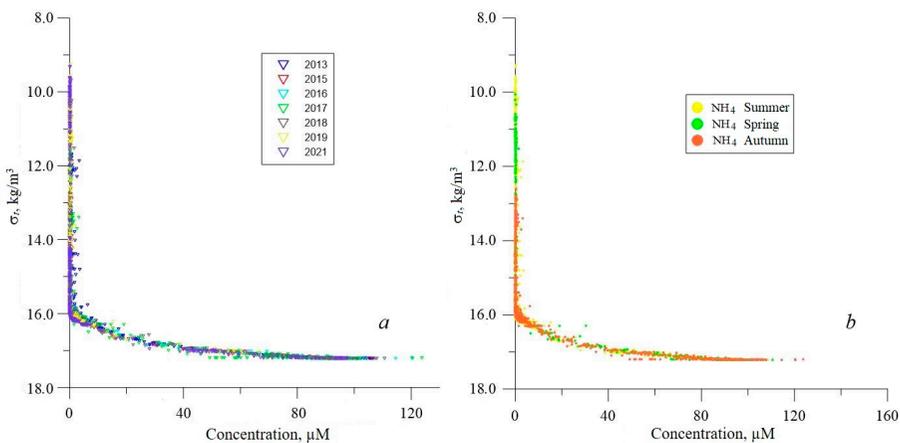

F i g. 12. Vertical distribution of ammonium at the density scale in 2013–2021(*a*) and by season (*b*)

In the spring-summer period, when greater heating of the waters is observed and stratification develops, the ammonium concentration in the aerobic zone is ~ 0.2 μM. With the beginning of autumn water mixing, the concentration of

seasonal variations, in contrast to nitrate nitrogen in the water layer, remain practically unchanged up to the boundary of hydrogen sulfide occurrence. The concentration of ammonium ions at a depth below 1800 m (σ_t = 17.0–17.2 kg/m^3) averages ~ 96 ± 5 μM, which is consistent with the previously obtained data [34, 37].

Phosphate. The averaged graphs of phosphate concentration dependence on density for different months were generally similar to each other (Fig. 13). Up to a density value of 14.0 kg/m^3, in almost all the cases the concentrations were close to analytical zero. Relatively minor increases were observed in July and August (up to 0.27 and 0.47 μM, respectively). The cause for this phenomenon may be an intensive plankton development during these months, accompanied by both the formation and lysis of cells resulting in the release of soluble phosphate.
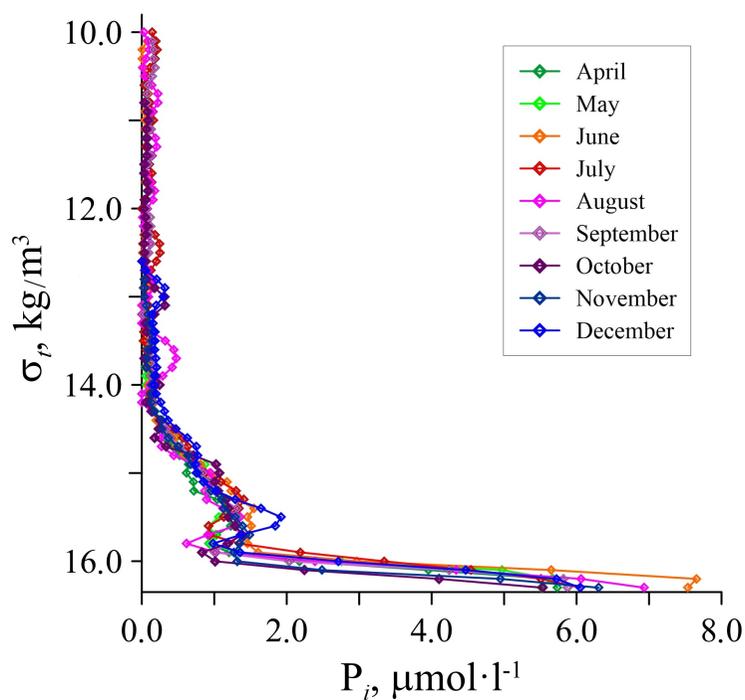
F i g. 13. Averaged vertical profiles of the phosphate content by month based on the data obtained in all the cruises in 2013–2017

The phosphate content after the oxycline occurrence at σ_t = 14.4–14.5 kg/m^3 gradually increases with depth, reaching concentrations of > 1 μM at σ_t = 15.5 kg/m^3. Then the concentration decreases and amounts to < 0.5 μM at σ_t = 15.8 kg/m^3, then monotonically increases to 6.5–8.0 μM on an isopycnic surface of 16.2 kg/m^3.

The development of the Black Sea eutrophication in the early 70s resulted in the rise of the maximum of phosphate, which in 1969 was located at the σ_t = 16.4 kg/m^3 and reached 6 μM, to a density of 16.2 kg/m^3 and its value increased to ~ 7.5 μM in 1990 [4, 38, 39]. Similar results were obtained in

2013, when the maximum phosphate concentration was 7.5 μM. That is, the maximum concentration of phosphate at the hydrogen sulfide zone boundary remains almost constant.

Carbonate system. Seasonal variability of carbonate system parameters of the northern part of the Black Sea is observed only in the upper part of the vertical profile (Figure 14, *a*, *b*) with density values of < 13 kg/m^3 for total alkalinity and < 14 kg/m^3 for pH, which corresponds to depths < 50 m. It is associated primarily with the processes of photosynthesis and organic matter decomposition, as a result of which carbon dioxide is removed or supplied from water, which transforms in water into the forms of bicarbonates and carbonates. In addition, seasonal pH variations in the surface waters are influenced by hydrological conditions (temperature changes) and the supply of carbonates with river discharge, as well as water exchange with the Sea of Azov through the Kerch Strait.
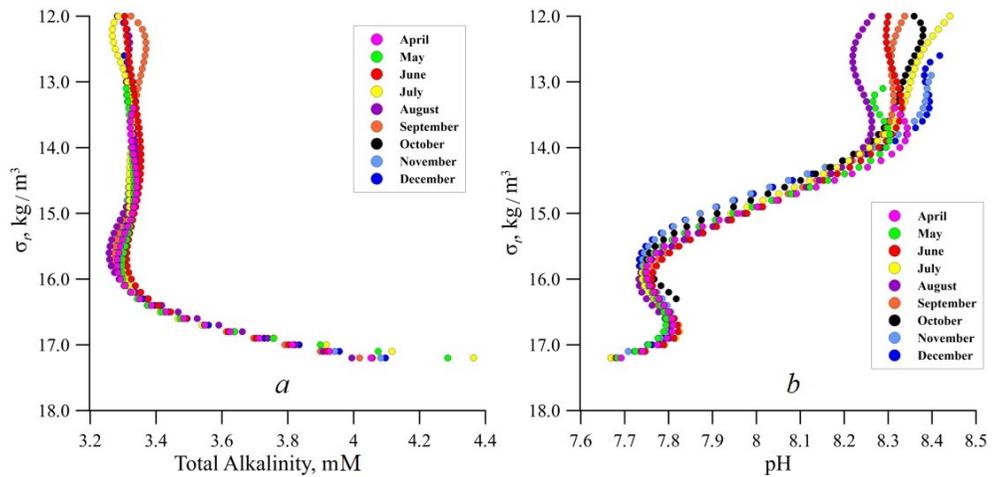
F i g. 14. Seasonal variability of the average values of total alkalinity (*a*) and pH (*b*) vertical profiles of the northern Black Sea waters based on the data obtained in 2013–2021

At a density of > 14 kg/m^3, a pH profile has an S-shape repeatedly confirmed throughout the entire research period (Fig. 14, *b*) [18], the presence of which can be explained by the entry of additional carbon dioxide into the deep-sea zone as a result of organic matter oxidation. At the same time, total alkalinity does not change up to a density of 16 kg/m^3, then it increases sharply (Fig. 14, *a*) due to the rise of carbonate alkalinity and a proportional increase in the ammonia and hydrogen sulfide components. This process occurs as a result of sulfate reduction according to the equation [8]

$$2SO_4^{2-} + 4C + 3H_2O \rightarrow H_2S + HS^- + CO_2 + HCO_3^-.$$

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[8] Alekin, O.A. and Lyakhin, Yu.I., 1984. *Chemistry of the Ocean*. Leningrad: Gidrometeoizdat, 344 p. (in Russian).

Conclusion

The work studied the spatial-temporal and vertical distribution of oxygen, hydrogen sulfide, carbonate system characteristics, as well as nutrients in the Black Sea waters in three hydrological seasons – spring, summer and autumn.

The study revealed that the distributions of the nutrients concentration in the sea surface waters demonstrated seasonality: for silicic acid there was a clear accumulation in spring; a feature of phosphate distribution was the unevenness between the deep-sea waters and the coastal waters in summer; nitrates were distributed relatively evenly in all seasons. Seasonal variability of total alkalinity showed a pronounced "sinusoidal" character with a minimum in the summer hydrological season and a maximum in the winter one. The minimum pH was observed in spring.

A decrease in the concentration of phosphate, silicic acid and inorganic forms of nitrogen was noted in the direction from coastal to deep-water areas of the Black Sea, which can be considered an indicator of manifestation of coastal sources of input.

River discharge is the predominant source of inorganic nitrogen and phosphorus input, as well as bicarbonates, into the Black Sea; atmospheric precipitation is the second most powerful source of such an input. At the same time, from our data we can conclude that precipitation on synoptic spatial-temporal scales can be the main source of inorganic nitrogen, phosphate and silicic acid entering the surface layer of sea waters in deep-sea areas.

The location of the suboxic zone upper boundary, determined by an oxygen concentration of 10 μM, varies over time from $\sigma_t = 15.7$ kg/m^3 to $\sigma_t = 15.9$ kg/m^3, which corresponds to an interval of ~ 40 m on the depth scale. The vertical distribution of hydrogen sulfide is more isopycnic – isosulfide 3 μM is located within $\sigma_t = 16.10$–16.15 kg/m^3.

The hydrogen sulfide content at depths > 1750 m in the Black Sea is currently 383 ± 2 μM.

The vertical maxima of nitrates were determined at a density $\sigma_t = 15.5$ kg/m^3. Interannual variations in the oxidized nitrogen content showed a decrease in absolute concentrations in the maximum layer to a level corresponding to pre-eutrophication indicators. The nitrates content was maximum (3.0–3.5 μM) in the period of 2013–2017. In subsequent years, maximum nitrate concentrations amounted to 1.8–2.6 μM.

The maximum phosphate content was observed at the boundary of the hydrogen sulfide zone.

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