Original Russian Text © S. I. Kondratev, A. V. Varenik, N. A. Orekhova, 2023,
published in MORSKOY GIDROFIZICHESKIY ZHURNAL, Vol. 39, Iss. 2 (2023)

Original article

Inorganic Forms of Nitrogen in the Deep Part of the Black Sea Based on the Expeditionary Data, 2016–2019

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Abstract

Purpose. The purpose of the study is to describe quantitatively the structure of vertical distribution of the nitrogen inorganic forms, namely nitrites, nitrates and ammonium ions, at the present post-eutrophication period of the deep-sea ecosystem evolution in the Black Sea based on the field data obtained in 2016–2019.

Methods and Results. The data obtained in the Black Sea within the economic zone of Russia in 2016–2019 by the scientists of Marine Hydrophysical Institute were used. At more than 200 deep-sea stations, a cassette of 12 bathometers (*Seabird-Electronics* CTD-instrument) was applied for taking hydrochemical samples at certain isopycnic surfaces, usually at σ_t = 16.30; 16.25; 16.20; 16.15; 16.10; 16.05; 16.00; 15.95; 15.90; 15.80; 15.50, 14.0 kg/m^3. Such a scheme permits to determine the suboxic zone locations (including its upper boundary), the depth of hydrogen sulfide formation, and also to study in detail the changes in the nitrogen forms during transition from the oxic conditions to the anoxic ones.

Conclusions. At the present post-eutrophication period of the deep-sea ecosystem evolution in the Black Sea, qualitative characteristics of the vertical distribution of inorganic nitrogen forms correspond to the already known features. The quantitative ones are characterized by the following values: from the surface to the oxicline onset near the isopycnic surface σ_t = 14.5 kg/m^3, the contents of nitrites and nitrates were at the level 0.06 μM and 2–3 μM, respectively, and the ammonium concentration did not exceed 0.6 μM. As for the nitrite vertical profiles, two maximums are noted at the isopycnic surfaces σ_t = 14.0 kg/m^3 and σ_t = 15.9 kg/m^3; the value of the second peak does not exceed 0.07 μM. The nitrate vertical profiles are characterized by a maximum within the range of isopycnic surfaces σ_t = 15.2–15.5 kg/m^3; its value reached 4–5 μM. The ammonium considerable concentrations were recorded at the isopicn σ_t = 16.0 kg/m^3, after which the ammonium content monotonously increased with depth reaching the value 96 ± 5 μM at the 2000-meter depth. The molar ratio NH_4^+/H_2S near the upper boundary of the hydrogen sulfide zone was 0.58 that indicated a significant equivalent excess of ammonium as compared to the theoretical stoichiometric value 0.30. At greater depths where the H_2S concentrations are high ($\geq$ 380 μM), it decreased to 0.25 and approached the theoretical value.

Keywords: Black Sea, hydrogen sulfide, nutrients, inorganic forms of nitrogen, vertical profile, field data

Acknowledgments: The investigation was carried out within the framework of the state assignments No. 0555-2021-0004 “Fundamental studies of the oceanological processes which determine state and evolution of the marine environment influenced by natural and anthropogenic factors, based on the observation and modeling methods” and FNNN 0555-2021-0005 “Complex interdisciplinary studies of oceanological processes that determine functioning and evolution of the ecosystems of coastal zones of the Black and Azov seas”, as well as with support of the RFFI project No. 21-55-52001.

For citation: Kondratev, S.I., Varenik, A.V. and Orekhova, N.A., 2023. Inorganic Forms of Nitrogen in the Deep Part of the Black Sea Based on the Expeditionary Data, 2016–2019. *Physical Oceanography*, 30(2), pp. 186-201. doi:10.29039/1573-160X-2023-2-186-201

DOI: 10.29039/1573-160X-2023-2-186-201

Introduction

Nitrogen is one of the most important elements needed for life on our planet. There is no shortage in it as 80% of the planet's atmosphere contains elemental nitrogen (N_2), but in the vast majority of cases, in order for nitrogen to be absorbed by plants, it must be in the form of ions available to them. These are ammonium (NH_4^+), nitrites (NO_2^-) or nitrates (NO_3^-), although some plants can also use molecular nitrogen for growth [1]. After the establishment of industrial production of ammonia in the early 20th century (the Haber process), nitrogen fertilizers began to be widely used in agriculture. Only 30–70% of them was absorbed by plants, and the rest was carried out by rivers into lakes or the ocean. Thus, it can be said that from about the middle of the 20th century the man himself began to "fertilize" lakes, seas and oceans with nitrogen compounds assimilated by phytoplankton [2].

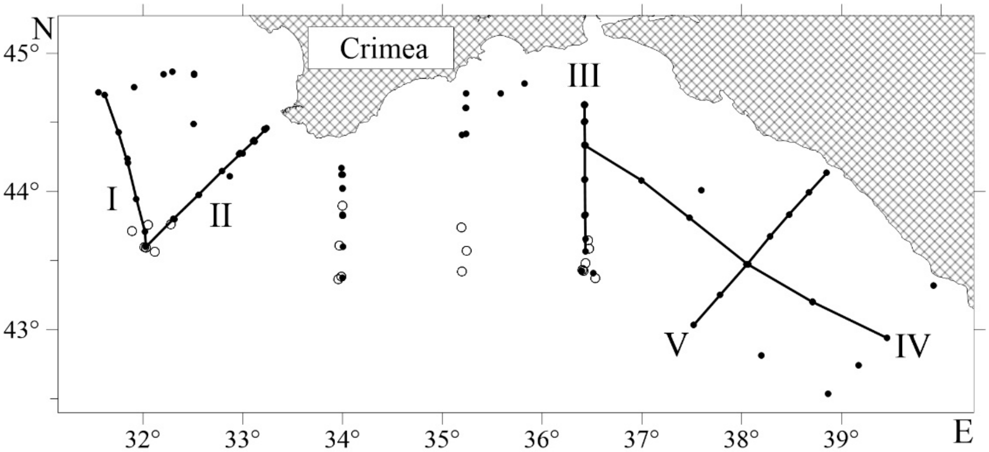
As a result, the so-called "red tides" started to occur in water bodies, when algae overgrown on the surface began to prevent sunlight from penetrating the water column, exchange of water with atmospheric oxygen, which ultimately leads to oxygen deficiency, development of hypoxia in the water and death of living organisms [3, 4].

For the Black Sea, the human impact was expressed in the fact that in the 60–70s the eutrophication period was observed, during which an additional amount of nitrogen compounds, as well as other nutrients entered coastal waters, organic matter production and supply constantly increased. At the same time, the molar ratio of nutrients Si:P:N changed, which was accompanied by toxin-producing algae development [5].

In the early 90s of the past century, the anthropogenic pressure on the Black Sea weakened, although it did not decrease to the "before eutrophication" level. The changes in the hydrochemical composition of the Black Sea waters in the periods "before", "during" and "after" eutrophication are considered in detail in [6–10]. In the same period, the network of the National Observation and Control System for Black Sea State Monitoring ceased to exist, single short-term cruises of the research vessels were carried out. From 1995 to 2015, only two expeditions were carried out with the Marine Hydrophysical Institute (MHI) participation – in 1995 on R/V *Professor Kolesnikov* and in 2004 on R/V *Akademik* of the Bulgarian Academy of Sciences. After 2015, the MHI expeditionary research in the Black Sea was resumed, and in 2016–2019, 11 cruises in the deep-water part were carried out. In these expeditions, the content of three main inorganic bound forms of nitrogen – nitrites, nitrates and ammonium ions was determined in sea water. In the Black Sea waters, at the boundary of the hydrogen sulfide appearance, formation of other forms of nitrogen is also possible, in particular, nitrous oxide and elemental nitrogen [11, 12], but they are not considered in this paper. The present research focuses on the quantitative description of the vertical distribution of nitrites, nitrates and ammonium ions in the deep-sea part of the Black Sea according to the data of expeditionary studies in 2016–2019 to provide representative quantitative characteristics of hydrochemical structure of the Black Sea waters in the modern period.

Materials and methods

The scheme of the deep-sea stations for the nitrites, nitrates and ammonium samplings in 2016–2019 in various hydrological seasons is shown in Fig.1.



F i g. 1. Scheme of the deep-sea stations for the nitrites, nitrates and ammonium samplings in 2016–2019 (solid lines indicate transects I – V, rhombuses – the stations where the samples were taken at 37 horizons)

The water samples for hydrochemical analysis were taken with a CTD 911 rosette of 12 5-1 Niskin bottles at certain densities. As a rule, the density σ_t was equal to 16.30, 16.25, 16.20, 16.15, 16.10, 16.05, 16.00, 15.95, 15.90, 15.80, 15.50 and 14.0 kg/m^3. At 19 stations, the sampling to determine the content of ammonium ions was carried out at 37 horizons: at the maximum probe immersion depth (up to 2,000 m), then in 100 m and along a number of densities given above. Such a sampling scheme allowed to determine the position of the upper boundaries of the intermediate suboxic layer and the hydrogen sulfide zone, as well as the details of the transition of oxidized forms of nitrogen into the reduced one when redox conditions change.

The samples obtained up to density σ_t = 16.3 kg/m^3 were filtered through membrane filters with a pore size of 0.45 μm then frozen at – 18 °C and delivered to the coastal laboratory for analysis by the spectrophotometric method for the content of the sum of nitrites and nitrates [1]. The determination was carried out on a flow autoanalyzer applying the method of reducing nitrates to nitrites using copper-plated cadmium. With a minimum detectable concentration of nitrates of 0.36 μM, the error of the method is ± 0.20 μM [2]. The determination of the content of nitrites and ammonium ions was carried out directly in the R/V onboard laboratory. To determine the concentration of nitrites, the method of Bendschneider

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[1] Rosgidromet, 2020. [*Mass Concentration of Nitrate Nitrogen in Sea Water. Photometric Measurement Technique after Reduction in a Cadmium Reducer: RD 52.10.745-2020*]. Effective from 22.02.2021 (in Russian).

[2] Committee for Hydrometeorology and the Monitoring of the Environment, 1993. [*Marine Chemical Analysis Guide: RD 52.10.243-293*]. Effective from 01.07.1993. St. Petersburg: Gidrometeoizdat, 264 p. (in Russian).

and Robinson [3] was used, to determine the concentration of ammonium ions – a modified Sagi – Solorzano method for sea water, based on the determination of an indophenol dye formed in an alkaline environment from phenol, ammonia and hypochlorite. Nitroprusside is used as a reaction catalyst in the method, which significantly increases its sensitivity [13], which is 0.05 μM [3]. Due to the high concentration of ammonium ions at depths below 500 m, the samples were diluted 10 times with water obtained at the same station as [a] dilution sample, from a depth corresponding to σ_t = 15.4 kg/m^3 (where the absence of ammonium ions is observed).

The hydrogen sulfide content was determined by the iodometric method, the iodine consumption at σ_t = 15.8 kg/m^3 was taken as zero in accordance with the work [4]. Fifteen minutes prior to sampling, 200 ml volumetric flasks were purged with argon.

Features of vertical profiles of nitrogen compounds in the deep Black Sea

The transition of some nitrogen compounds to others – nitrates to nitrites, nitrites to ammonium ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \rightarrow NH_4^+$) in the Black Sea is determined primarily by redox conditions, which primarily depend on the dissolved oxygen content [14, 15]:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \leftrightarrow 106CO_2 + 16HNO_3 + H_3PO_4 + 132H_2O, \quad (1)$$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 84.8HNO_3 \leftrightarrow 106CO_2 + 42.4N_2 + H_3PO_4 + \\ + 16NH_3 + 148.4H_2O, \quad (2)$$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 94.4HNO_3 \leftrightarrow 106CO_2 + 55.2N_2 + H_3PO_4 + 177.2H_2O, \quad (3)$$

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+, \quad (4)$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^-. \quad (5)$$

A large amount of fresh water enters the northwestern part of the sea with the flow of rivers (mainly the Danube, Dnieper and Dniester flow), and dense salty waters of the Sea of Marmara penetrate through the Bosporus at a depth of ~ 70 m [14]. The fresh water inflow from above and saline water from below leads to the formation of a permanent halocline in the Black Sea in the salinity range of 18.5–21.5 [15, 16]. This halocline, in turn, forms a pycnocline between the densities σ_t = 14.5 – 16.5 kg/m^3, which serves as a certain obstacle to the vertical exchange between surface and deep waters. Many authors have studied the spatial and vertical changes in hydrochemical elements in the Black Sea [17–19]. It should be noted that when considering the vertical distributions of the studied characteristics in the Black Sea, the depth scale is not used. For this purpose, the scale of density σ_t [15, 20, 21] is applied, which makes it possible to take into account the hydrological structure

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[3] Sapozhnikov, V.V., ed., 2003. [*Manual on Chemical Analysis of Marine and Fresh Waters in Environmental Monitoring of Fishery Reservoirs and the World Ocean Regions Prospective for Fishery*]. Moscow: VNIRO Publishing, 202 p. (in Russian).

[4] Bordovsky, O.K., ed., 1978. *Methods for Hydrochemical Studies in the Ocean*. Moscow: Nauka, 267 p. (in Russian).

influence on the occurrence depth of the characteristic features of the hydrochemical structure.

If there were no pycnocline in the Black Sea waters, then in winter almost 100% of oxygen-saturated cooled surface waters would penetrate to great depths due to their greater density, as it happens in most water bodies. However, for the Black Sea, the depth of the cooled surface water penetration (wherever they are formed – in the shelf areas or in the centers of cyclonic gyres) is limited by the depth of the cold intermediate layer (CIL) with a core at a depth of density σ_t = 14.5 kg/m^3 [22].

This limitation of the cooled water penetration depth leads to the renewal of the CIL during winter ventilation of the sea, which is the only source of oxygen for the deeper waters. The minimum CIL temperature (and, accordingly, the maximum oxygen content), which depends on meteorological conditions in winter, is located near σ_t = 14.5 kg/m^3. The constant oxygen consumption for the suspended organic matter (SOM) oxidation and the limited supply of O_2 only due to diffusion from the CIL leads to its gradual decrease with depth (oxycline appears) until it completely disappears, after which hydrogen sulfide appears. There is another source of oxygen in the Black Sea waters – the salty Sea of Marmara waters coming through the Bosporus. However, this oxygen is completely consumed for the hydrogen sulfide oxidation, which allows to keep the upper limit of hydrogen sulfide within σ_t = 16.1–16.2 kg/m^3 for the past 40 years [23].

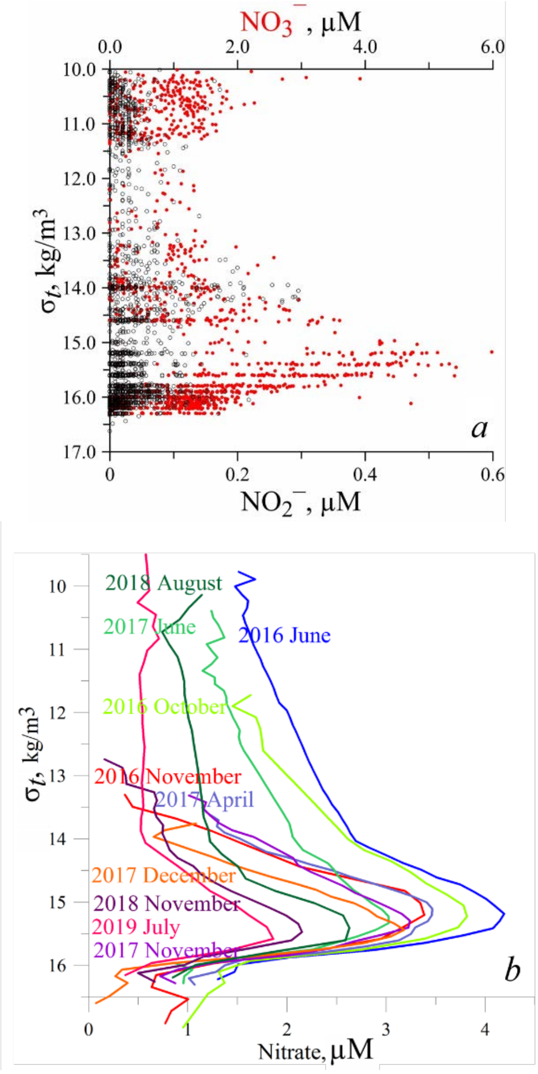
These dissolved oxygen distribution features affect vertical changes in the content of nitrogen compounds in the following way: in the upper productive layer of the Black Sea waters, which contains high concentrations of oxygen, the content of all forms of nitrogen is almost uniform in depth. In this layer, the SOM decomposition processes are compensated by the processes of photosynthesis and the accumulation of inorganic forms of nutrients (phosphorus, silicon, nitrogen) does not take place. The content of all these forms is relatively low compared to the concentrations of these compounds deeper than the CIL core by σ_t = 14.5 kg/m^3.

Starting approximately from the value of the density σ_t = 14.5 kg/m^3, the O_2 concentration decreases with depth. This means that the processes of oxygen consumption for the SOM oxidation prevail over the processes of its supply and the content of mineral forms of all nutrients increases. The vertical profiles of inorganic forms of each nutrient have their own characteristics. For nitrogen compounds, they differ in initial gradual increase of the content of nitrates, while the concentrations of nitrites and ammonium ions do not increase noticeably – until the oxygen contained in water is sufficient to oxidize the ammonium formed during the SOM decomposition to nitrates. This continues approximately until the moment when the O_2 concentration becomes less than 10–20 μM, corresponding to the upper limit of the so-called suboxic zone (SZ), located within the densities σ_t = 15.5–15.9 kg/m^3.

On the vertical profile of nitrates, the process of their accumulation during SOM mineralization ends with a wide maximum centered approximately at σ_t = 15.5 kg/m, after which (due to the lack of dissolved oxygen), the use of nitrates and nitrites as oxidizing agents begins in the processes of SOM decomposition and their concentrations decrease. In SZ, with a dissolved oxygen deficiency, when its concentrations slightly exceed the concentrations of nitrates and nitrites, the processes of interaction of various nitrogen forms can be observed, which end in the formation of molecular nitrogen and its reduced form. After the dissolved oxygen, nitrates, and nitrites, and then the oxidized forms of iron and manganese, are consumed for the SOM oxidation, a hydrogen sulfide zone appears, where the only inorganic bound form of nitrogen is ammonium, whose concentration monotonically increases with depth.

The obtained results and their discussion

The vertical profiles of oxidized forms of nitrogen in the deep Black Sea according to the data obtained in 2016–2019 are shown in Fig. 2.



F i g. 2. Averaged profiles of nitrites and nitrates for all the surveys in 2016–2019 (*a*), and those of nitrates for individual surveys in the same years (*b*)

In the vertical distribution (Fig. 2, *a*) there are two maxima of nitrite concentration at σ_t equaled to 14.0 and 15.9 kg/m^3, and the nitrate concentration maximum at σ_t = 15.2–15.5 kg/m^3.

From the surface to the upper boundary of the oxycline (σ_t = 14.5 kg/m^3), the ratio between nitrites and nitrates is ~ 1:10–20. At the same time, in the surface waters, the content of nitrites does not exceed 0.1 μM, while the content of nitrates in most cases is at least 1 μM (Fig. 2, *b*). At a depth corresponding to the density σ_t = 14.5 kg/m^3, there is an upper maximum of nitrites, which is probably determined by the fact that nitrites are an intermediate product during the SOM nitrogen transformation from a reduced to an oxidized state. Before the maximum concentration of nitrates is reached, the accumulation of nitrites is observed at the beginning of the oxycline layer [24] (Fig. 2, *a*).

Below this limit, the trends in the concentrations of these forms are different. The content of nitrates gradually increases in comparison with the layers where there is no oxygen deficiency (above σ_t = 14.0 kg/m^3), and a maximum is formed at σ_t about 15.2–15.5 kg/m^3 (sampling horizons do not allow to determine the maximum more accurately), which is the result of aerobic SOM degradation (equation (1)). Then, the concentrations of nitrates start to decrease rapidly with depth: when the oxygen concentration drops below 10 μM [25], denitrification reactions proceed (equations (2) and (3)), as a result of which the nitrates are withdrawn and the oxygen is no longer enough to oxidize ammonium ions coming from the underlying layers to nitrates [24, 26] (equations (4) and (5) [27]). In this case, an increase in the concentration of nitrites is observed (Fig. 2, *a*), since with oxygen concentration decrease, the nitrates should be reduced through the formation of nitrites to ammonium ions. On the other hand, the flux of ammonium from the underlying layers determines the course of the nitrification reaction (equations (4) and (5)), the intermediate product of which is also nitrites. The second maximum concentration of nitrites is observed at the upper boundary of the SZ.

Near the lower boundary of the SZ, corresponding to the density of the hydrogen sulfide appearance σ_t = 16.1 kg/m^3, the change in the content of nitrates, according to [20, 23] and our data, is ambiguous: at some stations they completely disappear, but in many cases their concentrations increase immediately below the boundary of the hydrogen sulfide appearance and can reach 1–2 μM, and only at σ_t = 16.3 kg/m^3 they decrease to analytical zero.

When considering the averaged nitrite profiles for individual surveys, it was found that in the layer of the lower maximum of nitrites (σ_t = 15.9 kg/m^3) their concentration is 2–3 times higher than that observed at higher horizons and reaches ~ 0.07 μM.

In 2016–2019 the maximum concentration of nitrates did not exceed 4 μM, while its deepening was noted (Fig. 2, *b*) from σ_t = 15.2 kg/m^3 (June 2016) to σ_t = 15.5 kg/m^3 (June 2019), which corresponds to the nitrate maximum limit in 1991 [15]. At the same time, the value of the maximum, which can be used to judge the intensity of primary production processes in the photic part of the sea [23], cannot be tied to a specific season. For example, in June 2016 it was the largest (~ 4 μM), and in July 2019 it was the smallest (~ 2 μM) (Fig. 2, *b*), which corresponds to the concentration in the pre-eutrophication period. Thus, a decrease in the average concentration of nitrates compared to the 1980s of the 20th century can be noted – during the eutrophication period of the Black Sea, it rose to 9–10 μM [23]. The change in the depth of nitrate maximum occurrence and their concentration dynamics may be due to changes in the phytoplankton structure [15, 28].

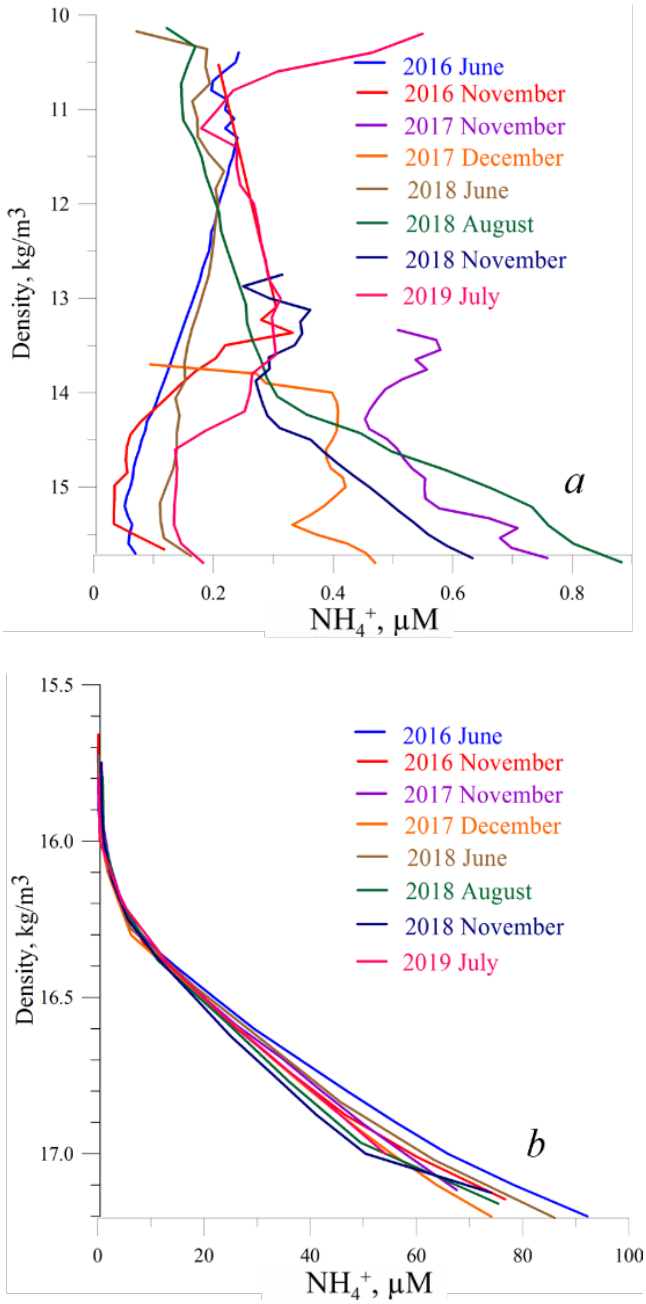


Fig. 3. Averaged ammonium profiles up to (*a*) and below (*b*) the hydrogen sulfide boundary in the 2016–2019 surveys

The dynamics of the concentration of ammonium is mainly determined by biogeochemical processes involving organic matter transformation and reactions with a conversion of mineral forms of nitrogen. Thus, the contribution of aerobic oxidation of SOM (equation (1)) to the ammonium production reaches 61%. In the anaerobic layer, SOM remineralization due to sulfate reduction contributes up to 30% to the production of ammonium [27]:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{2-} \rightarrow 106HCO_3^- + 53HS^- + 16NH_3 + H_3PO_4. \quad (6)$$

Another additional source of ammonium in the bottom waters is sediments [29]. However, in the aerobic zone, due to the oxygen presence, ammonium ions are oxidized to nitrates/nitrites (equations (4) and (5)), and this determines the relatively low concentrations of ammonium in this layer of water – they rarely exceed 0.5 µM and average ~ 0.22 µM. At the same time, the concentrations do not have a clear tendency to change after the oxycline appearance: in some cases, both an increase and a decrease can be observed, which is determined by the ratio of production-destruction processes. As the oxygen content decreases (in the layer of σ_t = 15.9 – 16.1 kg/m^3), the dynamics of ammonium ions is also determined by denitrification (equation (2)). A clear and rapid increase in the ammonium content starts below the boundary of the hydrogen sulfide appearance, at σ_t = 16.1 kg/m^3 (Fig. 3, *b*). Moreover, the concentrations already at σ_t = 16.3 kg/m^3 reach ~ 10 µM, which exceeds the total maximum concentrations of all forms of nitrogen in oxygen-containing waters.

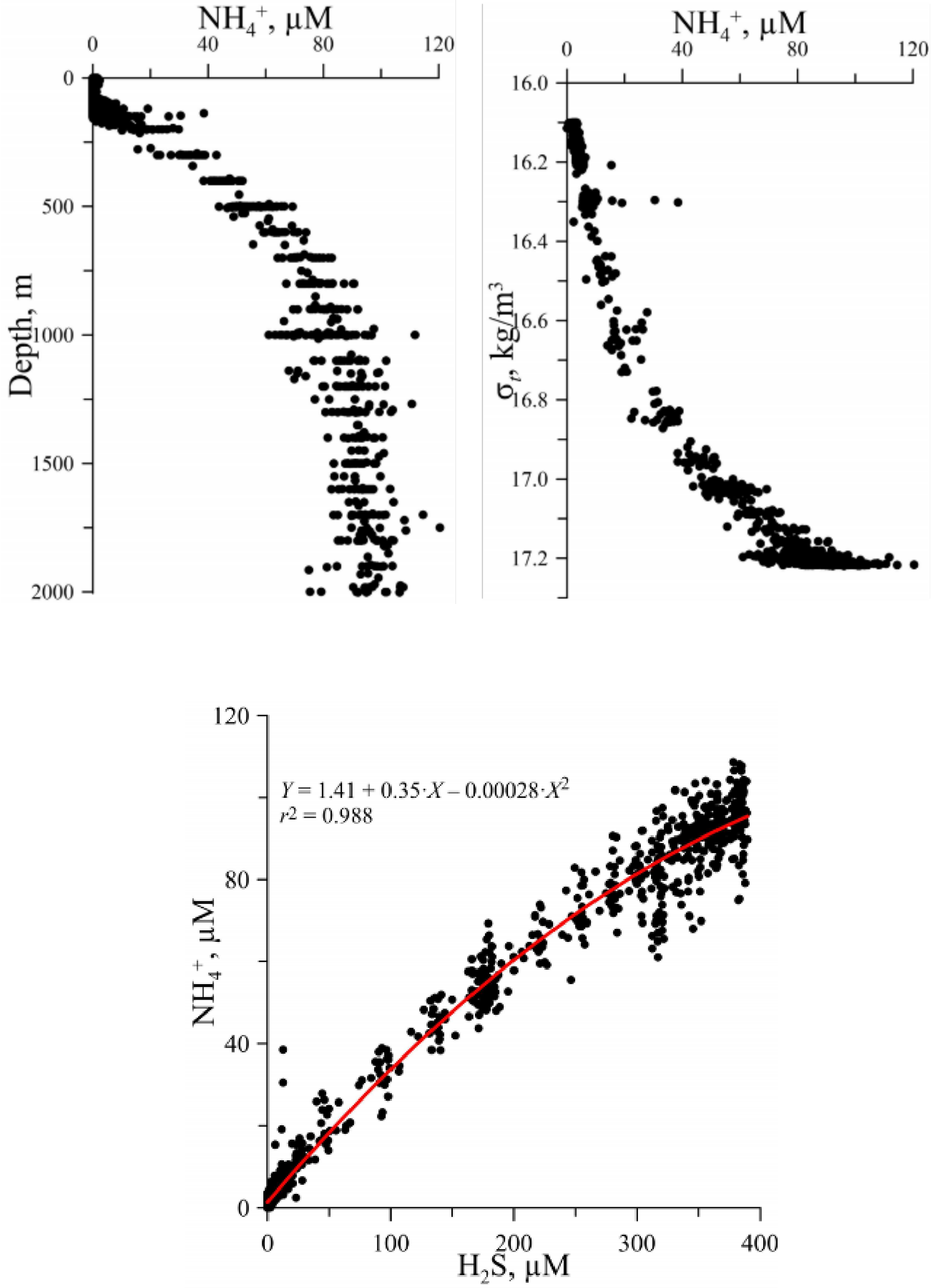
The concentration of ammonium ions at a depth of ~ 2000 m (σ_t = 17.0 – – 17.2 kg/m^3) averages ~ 96 ± 5 µM, which is consistent with the previously obtained data [15, 30].

The vertical ammonium profiles in the scale of depths and density for all the data obtained (Fig. 4, *a*, *b*) indicate a fairly large scatter of results, which in further studies will require methodological work to improve the ammonia determination methodology.

Since ammonium hardly oxidizes in the presence of hydrogen sulfide, the ratio of ammonium ions and hydrogen sulfide concentrations should be constant and, based on the stoichiometric ratio according to equation (6), equal to 0.30.

The observed changes in this ratio (Fig. 4) indicate a decrease in the relative content of ammonium ions during the transition from aerobic to anaerobic conditions. Thus, the molar ratio NH_4^+/H_2S, averaged by a polynomial (Fig. 4, *b*), gives, according to our data, the value 0.58 ± 0.14 for concentrations H_2S = 10 µM (31 values) and the value 0.25 ± 0.016 for concentrations $H_2S \geq 380$ µM (60 values).

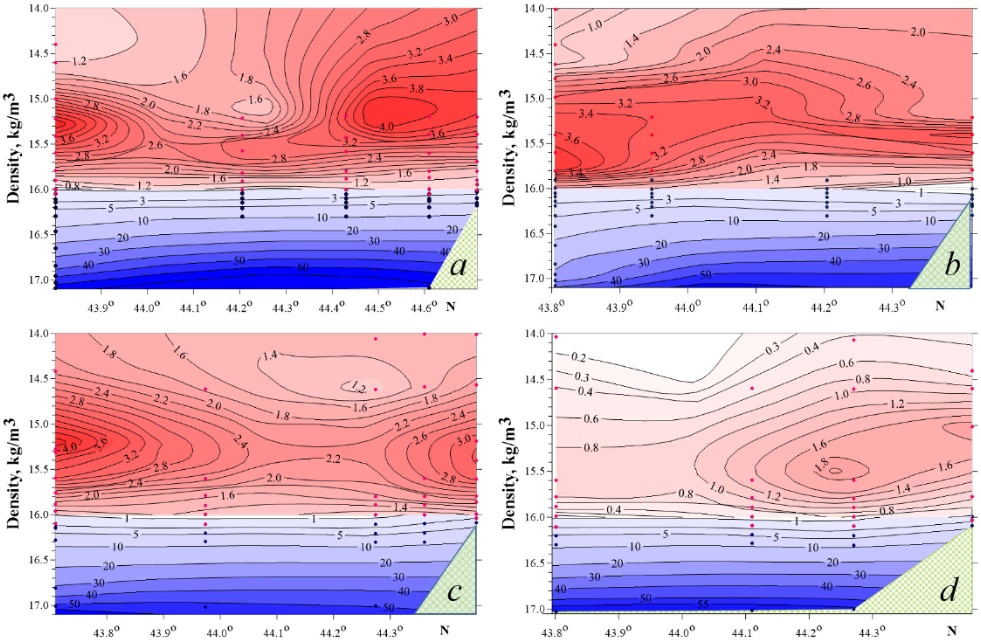
According to our data, at low H_2S (10 µM) concentrations, a significant excess of ammonium is observed in comparison with the theoretical values. This is due to the fact that up to 40% of the total amount of hydrogen sulfide oxidized in the Black Sea at these depths is actively oxidized due to horizontal flow of oxygen-enriched Bosporus waters [22]. However, at high concentrations of H_2S ($\geq$ 380 µM), the NH_4^+/H_2S ratio decreases to 0.25, which is close to the theoretical value. At the same time, a certain deficiency of ammonium ions can be noted in comparison with hydrogen sulfide.



F i g. 4. Vertical profiles of ammonium at the depth scale (*a*) and density (*b*), molar ratio NH_4^+/H_2S (*c*) in the Black Sea anaerobic zone in 2016–2019

Vertical profiles of nitrates and ammonium in five transects in the deep part of the Black Sea in 2016–2019

In Fig. 5–7 below, the simultaneous distribution of nitrates and ammonium ions in five transects marked in Fig. 1 are shown. To avoid crossing the nitrates and ammonium isolines, the distribution of nitrates was limited by the density $\sigma_t = 16.0$ kg/m^3, since, according to [24, 26], their concentration on this surface was close to zero.



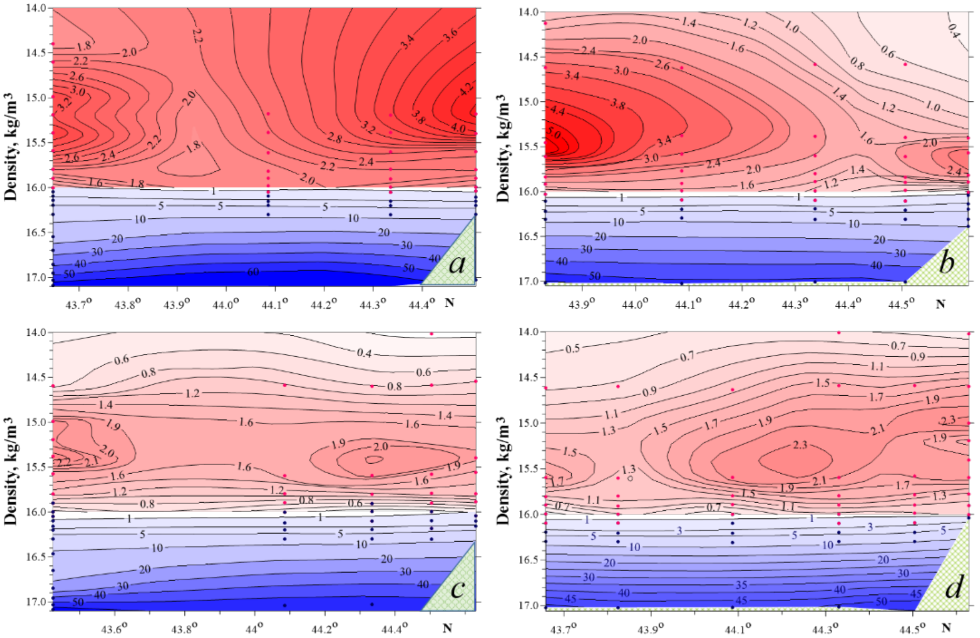
F i g. 5. Distribution of nitrates (red color) and ammonium (blue color) in transect I in June (*a*) and December (*b*), 2017, and in transect II in November, 2018 (*c*) and July, 2019 (*d*)

All transects are characterized by the appearance of ammonium having ~ 0.95 μM concentration at $\sigma_t = 16.0$ kg/m^3 and a monotonous content increase with depth, which qualitatively resembles hydrogen sulfide distribution. For nitrates, such an isopycnic distribution along the vertical is not typical. On all profiles in some areas, their maximum concentrations are observed in the range of $\sigma_t = 15.3 – 15.5$ kg/m^3, not exceeding 5 μM, however, these maxima cannot be tied to seasons or geographic location. Thus, in transect I, perpendicular to the northwestern shelf (Fig. 5, *a*, *b*), the maximum concentrations in June and December 2017 were approximately the same, while in June they were observed over the shelf part of the section, in December – in deep water areas. In trasect II Cape Chersonesos – the Bosporus (Fig. 5, *c*, *d*), the maximum of nitrates in November 2018 was located in the deep-sea part, in July 2019 – in the shelf part.

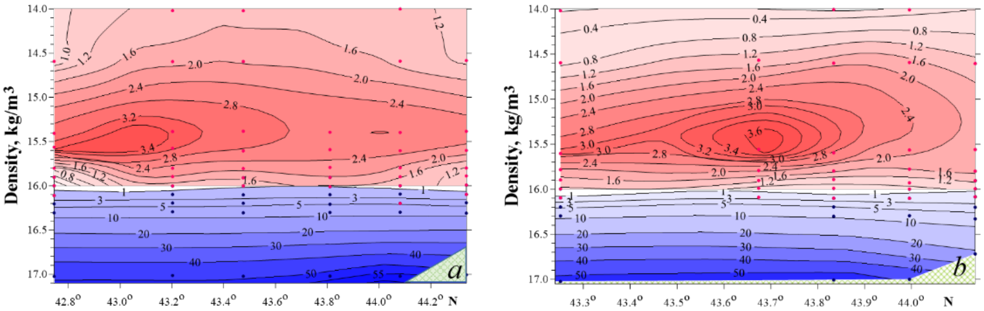
In the Kerch transect III, the nitrate maximum observed in the shelf part in June 2017 noticeably decreases in August 2018 (Fig. 6, *a*, *b*), and this decrease in concentration continues in November 2018 and July 2019 (Fig. 6, *c*, *d*). Moreover, in the latter case, the distribution of nitrates for two different hydrological seasons turned out to be very similar.

In the eastern part of the sea in August 2018, in transect IV, the maximum of nitrates was located in the deep-sea area (Fig. 7, *a*). All stations of transect V were located along the eastern coast at approximately the same depth; in July 2019, the nitrate maximum was observed only in the middle of this transect (Fig. 7, *b*).

Such distribution of nitrates in the transects is most likely associated with the peculiarities of water dynamics.



F i g. 6. Distribution of nitrates (red color) and ammonium (blue color) in transect III in June, 2017 (*a*), August (*b*) and November (*c*), 2018, and in July, 2019 (*d*)



F i g. 7. Distribution of nitrates (red color) and ammonium (blue color) in the eastern part of the Black Sea in transect IV in August, 2018 (*a*) and in transect V in July, 2019 (*b*)

Conclusions

In the present paper, the data obtained during 11 expeditions of the Marine Hydrophysical Institute in the Black Sea (the economic zone of Russia) in 2016–2019 was considered. Based on the analysis of data on the vertical distribution of inorganic nitrogen forms (nitrates, nitrites and ammonium ions) from the surface to a depth of 2,000 m, it was established:

1. From the surface to the start of oxycline, near $\sigma_t = 14.5$ kg/m^3, the concentrations of nitrites and nitrates were at the level of 0.06 and 2–3 μM, respectively; the ammonium content did not exceed 0.6 μM. The dynamics of the concentration of mineral forms of nitrogen was determined mainly by aerobic SOM oxidation, as well as by nitrification, i.e., oxidation of ammonium ions to nitrates.

2. The vertical profiles of nitrites are characterized by the presence of two maxima in σ_t, equal to 14.0 and 15.9 kg/m^3. The vertical distribution of nitrites is determined by the processes of nitrification in the aerobic waters and denitrification in the suboxic zone.

3. The vertical profiles of nitrates are characterized by concentration increase, starting from $\sigma_t = 14.2 – 14.5$ kg/m^3. The maximum concentration was observed in the range of densities $\sigma_t = 15.2 – 15.5$ kg/m^3 and did not exceed 4–5 μM. A decrease in the concentration of nitrates near the boundary of the hydrogen sulfide occurrence ($\sigma_t = 16.1$ kg/m^3) is also the result of denitrification with the molecular nitrogen formation. In this case, the accumulation of nitrites takes place.

4. The appearance of ammonium with 0.95 μM concentration was recorded at $\sigma_t = 16.0$ kg/m^3, then their content increased monotonically, reaching 96 ± 5 μM at the 2,000 m depth.

5. The molar ratio NH_4^+/H_2S near the upper boundary of the hydrogen sulfide zone at concentrations of H_2S = 10 μM turned out to be 0.58; here, an excess of ammonium ions compared to sulfides is observed. At greater depths at high concentrations of H_2S ($\geq$ 380 μM), it decreased to 0.25 and approached the theoretical value of 0.30.

6. No pronounced regularities in the spatiotemporal distribution of nitrates and ammonium ions along the transects from the northwestern to the eastern Black Sea area have been identified. The maximum concentrations of nitrates cannot be tied either to the season or to the geographical location.

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The authors have read and approved the final manuscript.
The authors declare that they have no conflict of interest.