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Oxygen Dynamics during the Period of Dystrophic Processes in the Black Sea

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Purpose. The paper is aimed to analyze (i) peculiarities of the oxygen content and distribution in the Black Sea waters and (ii) the ratio of the observed changes in the oxygen distribution, the total primary production level and changes in the cold intermediate layer ventilation.
Methods and Results. The expedition data (2015–2019) as well as the data array (1980–2013) from the Oceanographic Data Bank of Marine Hydrophysical Institute, RAS, were used to analyze the oxygen content. The data for the deep part of the Black Sea (exceeding the 200 m depth) were selected. To analyze the primary production values, the shipboard fluorometric measurements of the chlorophyll *a* concentrations (1980–2001), and also the surface chlorophyll *a* concentrations derived from the *SeaWiFS* and *MODIS-Aqua* color scanners remote sensing (1998–2019) were utilized. The primary production was calculated using the regression equations in the form $y = a + bx$ that bound up the primary production in the water column with the surface chlorophyll concentration. The calculated data reveal a significant increase in the annual primary production level (to 400 g C/m^2·year) in the first half of the 1980s, then it declined on the average to ~ 140 g C/m^2·year from 1985 to 1995, and it remains at the level of ~ 100 g C/m^2·year from 1998 up to the present time. These variations in the primary production values correspond to the observed changes in the vertical distribution of nitrate and an increase in the temperature of the cold intermediate layer core, resulting in a decrease of the oxygen concentration in the deep oxic layers.
Conclusions. An increase in temperature in the upper layers of the sea and a reduction of the winter convective mixing intensity resulted in a decrease in the oxygen supply to all layers of the aerobic zone of the Black Sea. The lowest oxygen content recorded for the whole period of 1980–2019 was revealed in 2010. At the same time, dystrophication process drove the Black Sea system to its natural state, when the oxygen content dynamics depended mainly on the intensity of physical ventilation.

Keywords: oxygen, oxygen concentration, eutrophication, primary production, cold intermediate layer, Black Sea

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Introduction

Dissolved oxygen is one of the most important hydrochemical components that ensure vital conditions for living organisms in the water column. Oxygen in the seawater is necessary for the following oxidative processes: respiration of living organisms and oxidation of organic and reduced inorganic substances of natural and anthropogenic origin. As for the entire World Ocean [1], the Black Sea [2, 3] is characterized by a decreasing oxygen content, however, the input and priority of biogeochemical and physical processes remains a debatable issue [2, 4]. This issue is especially important for the Black Sea since its waters contain hydrogen sulfide in deeper layers, and physical, biochemical, biological, and hydrodynamic processes in the upper, a rather thin layer (up to 150–180 m), are responsible for the oxygen content and depth penetration.

The oxygen budget in the water column is determined by the ratio of the input and output processes. In the case of a balance of supply and consumption and unchanged intensity of hydrodynamic processes, the oxygen distribution remains stable. Oxygen enters the water column from the atmosphere and due to process of photosynthesis, and then it penetrates depleted layers due to exchange hydrodynamic processes. Oxygen is consumed in respiration, as well as for oxidation of organic substances and reduced forms of iron, manganese, nitrogen compounds, etc. The main source of organic matter in the seawater is primary production of phytoplankton due to photosynthetic processes in the euphotic layer, where organic compounds are synthesized from CO_2. One of the most important parameters making possible to evaluate the phytoplankton biomass and to calculate primary productivity is the concentration of chlorophyll *a* in the surface layer of the sea [5]. Satellite observations make possible to study variations in chlorophyll *a* in the surface layer over a wide range of spatial and temporal scales.

The oxygen reserve in the aerobic zone below the upper mixed layer is determined by the intensity of winter convection and processes of transformation of the Mediterranean waters, which ensure the oxygen supply to the layers of its maximum penetration, and the intensity of its consumption in redox biogeochemical and biological processes.

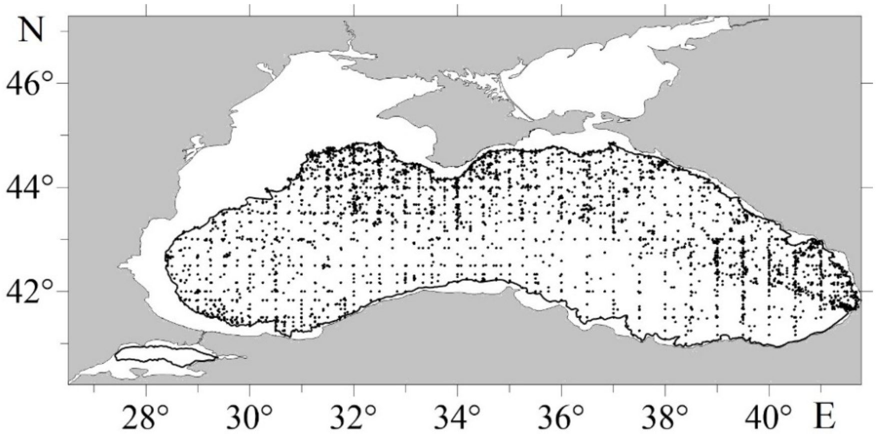
It was demonstrated in publications before 2010 (for example, [6]) that the observed decrease in the oxygen content in the Black Sea waters was associated quantitatively with an increase in the flux of organic carbon. The effect of this flux could not be balanced even by the observed decrease in temperature and an increase in the intensity of physical ventilation. All the more surprising were the results of the continuing decrease in the oxygen content after the completion of eutrophication in the Black Sea [7], and then in the process of reducing the Black Sea eutrophic level (dystrophication) [2–4].

The purpose of this work is to re-consider the content and distribution of oxygen in the Black Sea waters, as well as to analyze the relationship between the observed changes in the oxygen distribution, the level of primary production, and changes in the temperature regime and ventilation of the cold intermediate layer (CIL).

Materials and methods

Data on the content and distribution of oxygen in the Black Sea waters in 2015–2019 were obtained in expeditions of Marine Hydrophysical Institute (MHI) of RAS in the northwestern, northern, and northeastern parts of the Black Sea

(Fig. 1). For an earlier period of 1980–2013, the data were used from the MHI Oceanographic Data Bank [8].



F i g. 1. Location of oceanographic stations (sampling locations) for the research period of 1980–2019. The solid line is the 200 m isobath

Dissolved oxygen was determined by the method of volumetric Winkler titration modified by Carpenter [9]. The method is based on chemical reactions that convert dissolved oxygen into an equivalent amount of iodine, which is subsequently titrated. In order to eliminate contamination of samples with atmospheric oxygen, water from low oxygen layers was sampled into dried, argon-purged narrow-necked flasks. The technique allows us to obtain results with the accuracy of ±0.010 ml/l (±0.4 μmol/l).

The Weiss formula [10] was used to calculate the oxygen saturation (%):

$$\ln C = A_1 + A_2\,(100/T) + A_3 \ln (T/100) + A_4\,(T/100) + \\ + S\,[B_1 + B_2\,(T/100) + B_3\,(T/100)^2], \quad (1)$$

where C is the oxygen solubility (ml/l) at the pressure of 1 atm; $A_{(1,2,3,4)}$ and $B_{(1,2,3)}$ are constants: $A_1 = -173.4292$; $A_2 = 249.6339$; $A_3 = 143.3483$; $A_4 = -21.8492$; $B_1 = -0.033096$; $B_2 = 0.014259$; $B_3 = -0.0017$; T is the absolute temperature, K; S is the salinity value, ‰.

Data were selected for analysis from the deep part of the Black Sea (with depths of more than 200 m). The spatial distribution of sampling locations for 1980–2019 is demonstrated in Fig 1.

Some values of the oxygen concentration, which were characterized by random emissions and did not correspond to similar features in the distribution of other hydrological and hydrochemical parameters, were removed from the data set for analysis. The average profiles of temperature, salinity, oxygen concentration, water saturation with oxygen, and nitrate concentration were retrieved on the scale of density. Data were averaged by the method of inverse distances followed by additional smoothing by the low-frequency filtering method [11].

Since the distribution of hydrochemical parameters in the deep part of the water column is highly isopycnal throughout the year, except for special cases of intense winter ventilation [12–15], hydrochemical data can be averaged over the entire sea area and for time intervals using the density instead of the depth scale.

Data from shipboard measurements of chlorophyll *a* obtained by the fluorometric method for 1980–2001, as well as the data on the surface concentration of chlorophyll *a* obtained using remote sensing with SeaWiFS and MODIS-Aqua color scanners for 1998–2019, were used to calculate the primary production values. The chlorophyll *a* concentration in the sea surface layer was calculated using the NASA Ocean Biogeochemical Model, abbr. NOBM (https://giovanni.gsfc.nasa.gov/giovanni/).

They demonstrated [16–21] a high correlation between the shipboard measurements of chlorophyll *a* concentration and off-shore satellite data in the Black Sea. The correlation coefficient for the entire data set was 0.94–0.96 indicating a strong correlation between the measured and calculated chlorophyll *a* concentrations.

According to published data [17–21], the chlorophyll *a* concentrations obtained using the standard NASA algorithm were overestimated 1.7- to 2.1-fold. Therefore, the data on the chlorophyll *a* concentration, retrieved from the *Giovanni* resource (https://giovanni.gsfc.nasa.gov/giovanni/), were corrected.

The primary production values were calculated following the equation y = a + + bx (proposed by A. B. Demidov [22]), making the primary production in the water column a linear function of the surface chlorophyll concentration (Table).

The correlation coefficient (0.69–0.87) for the regressions in the table was highly significant ($p < 0.01$) [22].

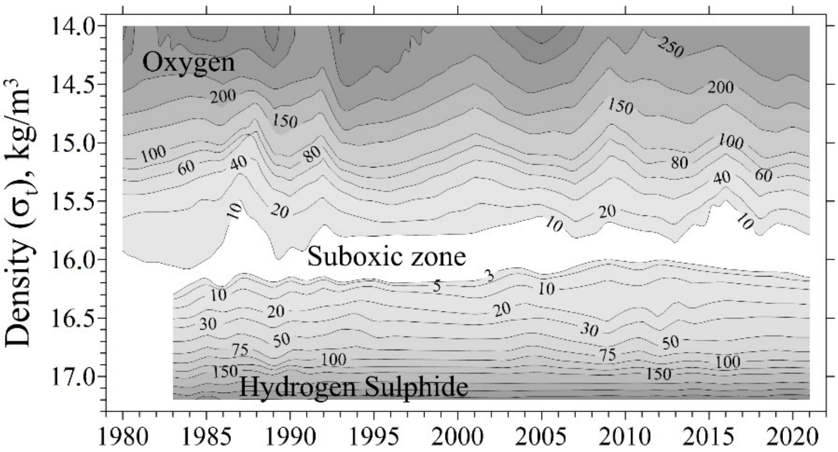
Regression equations ($y = a + bx$) binding up the primary production in the water column (C_{phw}, mg C/m^2 per day) with the surface chlorophyll concentration (C_{chls}, mg/m^3) based on [22]

Month	*y*	*x*	*a* ± *S. E.*	*B* ± *S. E.*	*N*	*r*	*m*	*F*
IV V	lgC_{phw}	lgC_{chls}	2.614 ± 0.025	0.511 ± 0.039	62	0.863	0.188	2.377
VI VII VIII IX	lgC_{phw}	lgC_{chls}	2.751 ± 0.021	0.498 ± 0.029	99	0.868	0.188	2.377
X XI	lgC_{phw}	lgC_{chls}	2.518 ± 0.024	0.532 ± 0.056	46	0.818	0.162	2.109
XII I II III	lgC_{phw}	lgC_{chls}	2.581 ± 0.013	0.600 ± 0.052	149	0.693	0.149	1.986

N o t e: *S. E.* is a standard error of the absolute term *a* and the regression coefficient *b*; *N* is the number of measurements; *r* is the correlation coefficient; *m* is the regression error; *F* is the variability indicator *y* at a certain *x*.

Results and discussion

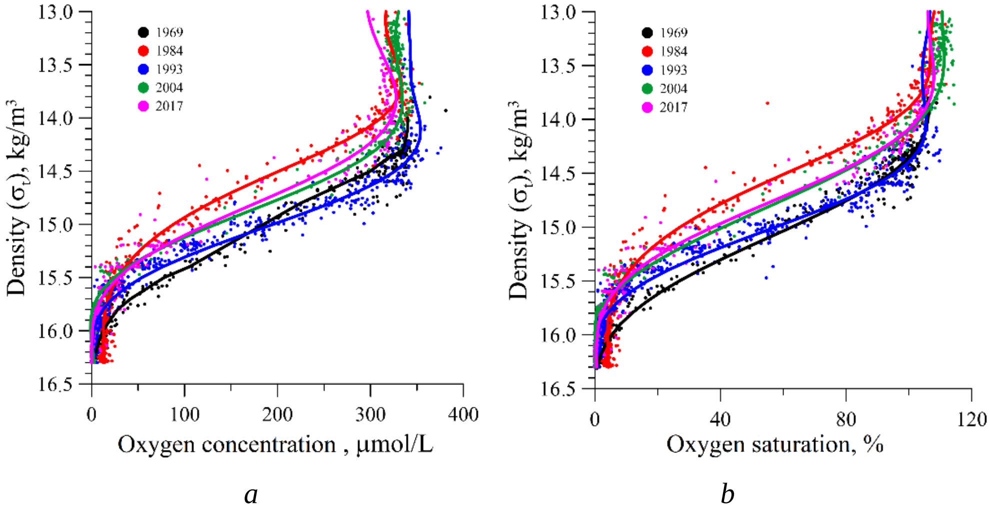
The distribution of oxygen and hydrogen sulfide versus density in the Black Sea waters over the last 40 years is demonstrated in Fig. 2. The mid-1980s were characterized by low temperatures of the CIL and high intensity of its ventilation [23, 24], as well as a high level of cold content [4], supporting a high level of oxygen supply. However, the traced increase in the level of primary production during this period led to the oxygen consumption in oxidation of the increased organic matter flux. As a result, the upper boundary of the suboxic zone, determined by the position of iso-oxygen 10 μmol/l, began to shallow and was located at the density of $\sigma_t = 15.6$ in 1987 (Fig. 2).



F i g. 2. Location of the suboxic zone boundaries in the deep part of the Black Sea

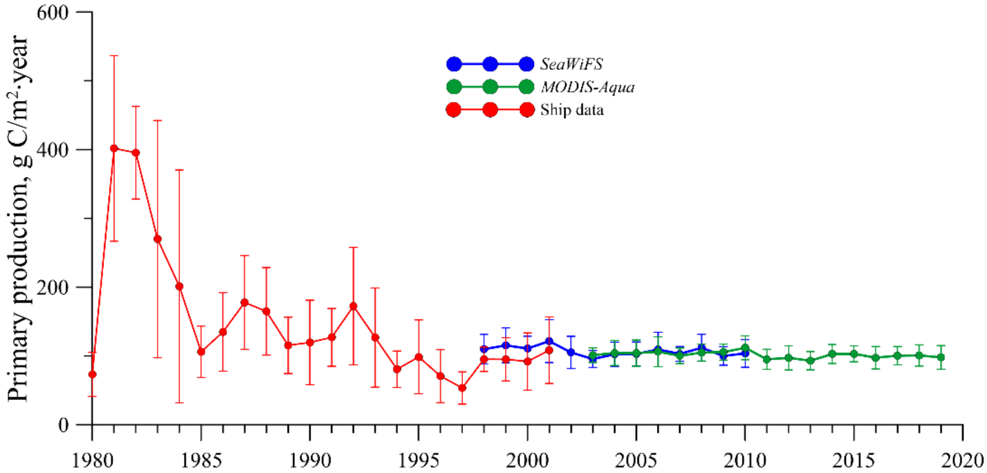
Then several cold winters of the late 1980s – early 1990s resulted in deepening of the upper suboxic boundary to the isopycnal surface of $\sigma_t = 15.8$. Following fluctuations in the position of the upper suboxic boundary could be due to both changes in the primary production values and intensity of physical ventilation. In 2005, the CIL was characterized by a low renewal rate [25], which led to a shallow location of the suboxic boundary. The very strong CIL ventilation in 2012 caused deepening of the suboxic boundary to $\sigma_t = 15.85$. In following years (2013–2015), the intensity of ventilation was below the average climate values, which contributed to the suboxic boundary at $\sigma_t = 15.5$ in 2015.

A significant decrease in the oxygen concentration in the layer of oxycline was traced until the mid-1980s (Fig. 3). That was explained by an increase in the flux of organic matter from the photosynthesis zone due to an increase in the primary production of phytoplankton [6, 26], which reached its maximum value by the beginning of the 1990s. [27]. However, cold winters of the early 1990s [4, 23, 24] led to an increase in the vertical gradient and, as a result, an increase in the oxygen flux to and its concentration in the oxycline (Fig. 3). A further decrease in the oxygen concentration in the main pycnocline could be associated with both an increase in primary production [7] and a decrease in the ventilation intensity and an increase in the water temperature [3, 4].



F i g. 3. The vertical distribution of the oxygen concentration (*a*) and the level of water saturation with oxygen (*b*) in the deep part of the Black Sea (solid lines indicate the average profiles for individual expeditions)

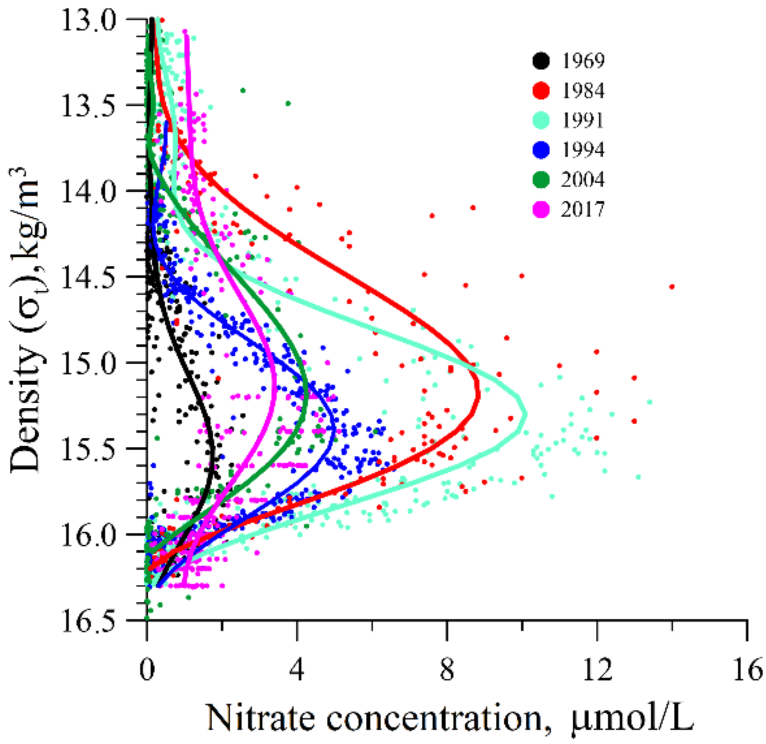
The oxygen flux to the main pycnocline of the Black Sea and the position of the upper boundary of the suboxic zone depend on the rate of organic matter oxidation and the intensity of water convective ventilation in winter. According to our data on the annual primary production, there was a significant increase up to 400 g C/m^2·year in the first half of the 1980s, then it decreased to an average of ~ 140 g C/m^2·year from 1985 to 1995, and it remained at ~ 100 g C/m^2·year level after 1998 (Fig. 4). These data were in good agreement with inter-annual variations in the annual primary production in publications [22, 27].



F i g. 4. The average annual value of primary production for the deep part of the Black Sea based on satellite data (standard deviation is shown for each point)

Primary production processes generate the export flux of organic matter below the euphotic zone. These processes determine incorporation of carbon and nutrients into biochemical cycles of marine ecosystems.

According to published data [28–30], a significant input of nutrients to the Black Sea with the river runoff in the 70s–80s led to an increase in the intensity of primary production processes (eutrophication), an increase in the flux of particulate organic matter from the euphotic layer to the deeper layers of water, intensive oxygen consumption (see Fig. 3) and an increase in the concentration of nitrate in their maximum in the pycnocline by more than four times [6, 31] (Fig. 5). Vertical convection in the water column intensified from the mid-1980s – early 1990s due to a number of cold winters [6, 32]. This contributed to significant shoaling of the main pycnocline [33], and subsequently to an increase in the turbulent and advective input of nutrients from deeper layers through the CIL to the euphotic layer [31]. These processes led to intensive bloom of phytoplankton and the organic matter production in the deep part of the Black Sea. However, by the early 2000s [30], a decrease in the flux of nitrogen compounds with riverine waters led to a decrease in the content of nitrate in the main pycnocline layer and a decrease in the influence of biogeochemical processes of oxygen consumption on its content and distribution in seawaters.

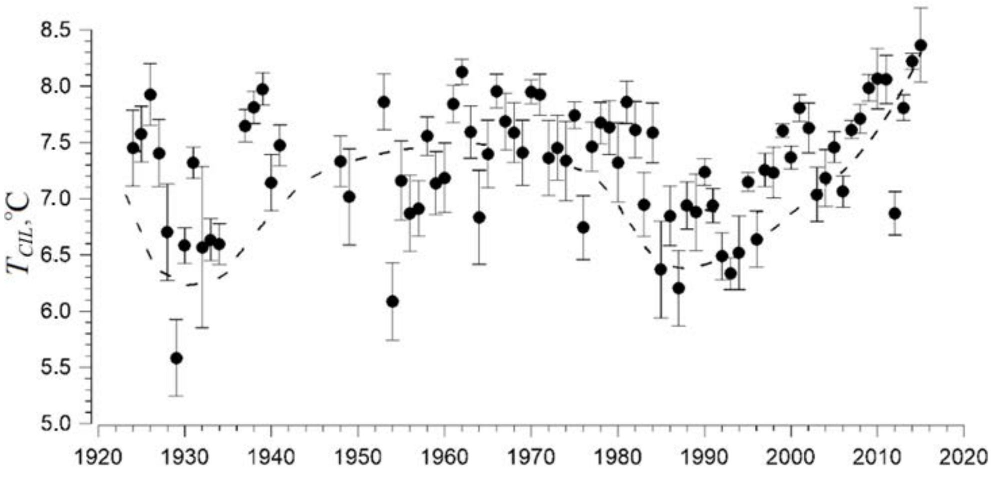


F i g. 5. The vertical distribution of the nitrate concentration based on the multi-annual data (the lines indicate the average profiles for individual expeditions)

It can be seen in Fig. 5 that the maximum concentration of nitrates was 2–3 µmol/l in the late 1960s. It increased, on average, about four-fold and averaged ~ 8 µmol/l by the mid-1980s. In the early 1990s, the concentration of nitrate was within the range of 9–10 µmol/l. Then there was a decrease in the maximum concentration to ~ 5 µmol/l in 1994 and it remained almost unchanged by 2004. In the last decade, the concentration of nitrate in the layer of the maximum decreased further to 2–3 µmol/l by now (Fig. 5).

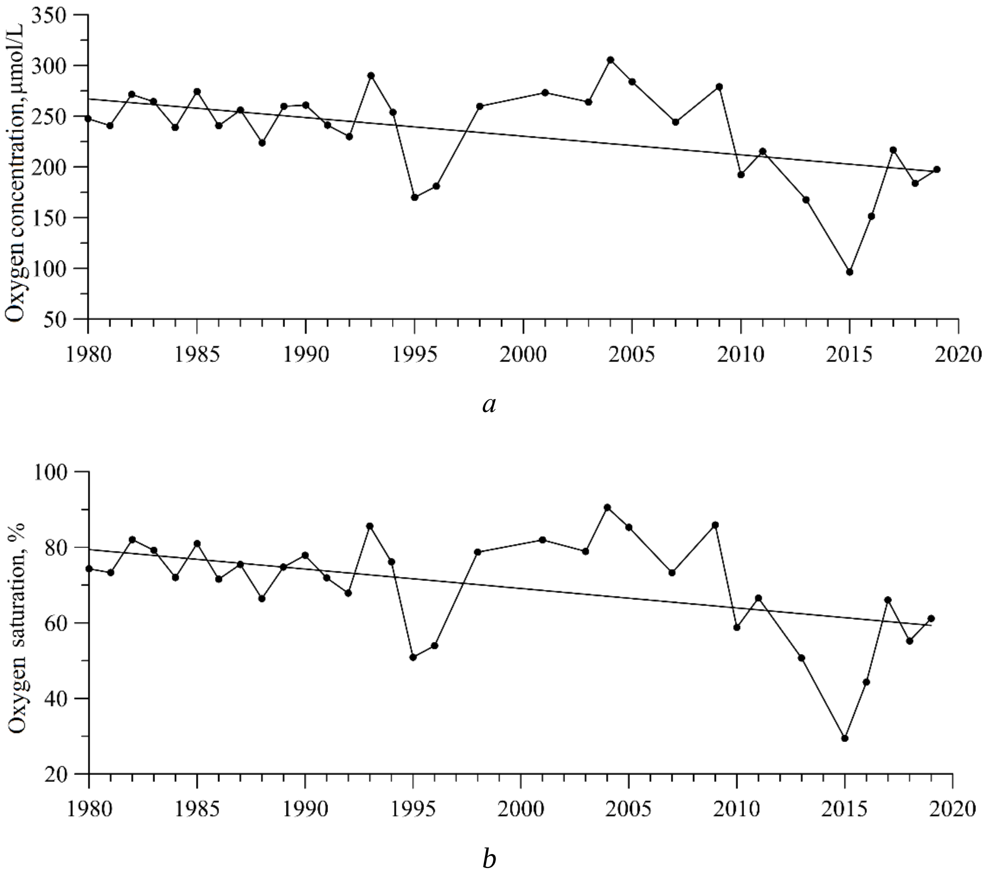
Thus, available data on the dynamics of primary production (Fig. 4) and the vertical distribution of nitrate in the main pycnocline layer (Fig. 5) show that biogeochemical processes are characterized by constancy and low intensity as compared to the period of eutrophication in the 1980s. As the result, the dynamics of the oxygen distribution in the modern period should be largely determined by changes in the water ventilation intensity, primarily in winter.

According to published data [23, 34, 35] on changes in thermohaline characteristics of the upper Black Sea waters, an increase in the sea surface and the cold intermediate layer water temperatures by 1–1.5 °C took place in 2001–2008. According to [23], the maximum CIL temperature according to the winter data was observed in the 1960s and in 2001–2008, the minimum – in the 1980s. The summer temperature in the CIL did not exceed 8 °C up to 2008. From the 1970s to the 1990s, the volume of the CIL waters increased and its core was observed closer to the sea surface (by 10 m over the sea). At the same time, the temperature in the core of the CIL dropped below 7 °C. In the 1990s, the highest position of the CIL upper boundary was traced at 40 m. Since the mid-1990s, the water temperature in the CIL increased. According to our data, the average temperature of the CIL core waters exceeded 8 °C after 2008 (Fig. 6).



F i g. 6. The temperature in the CIL core based on the primary data averaged over the period May – November [25]. Segments show the dispersion of the values corresponding to ±1 standard deviation, the dashed line corresponds to the polynomial approximation *b*

The reduced intensity of the CIL water renewal [25] and the decrease in their cold content [4] from 2008–2019 lead to a decrease in the oxygen concentration in the CIL core (Fig. 7) in the 1980s – early 1990s and in the post-eutrophication period in the late 1990s – early 2000s, the oxygen concentration was relatively stable and fluctuated within 250 ± 25 µmol/l, and the degree of water saturation with oxygen was 70–80%. After 2005, a gradual decrease in the oxygen concentration to 175 ± 25 µmol/l and in the degree of saturation to 40–60% were observed in the CIL core.

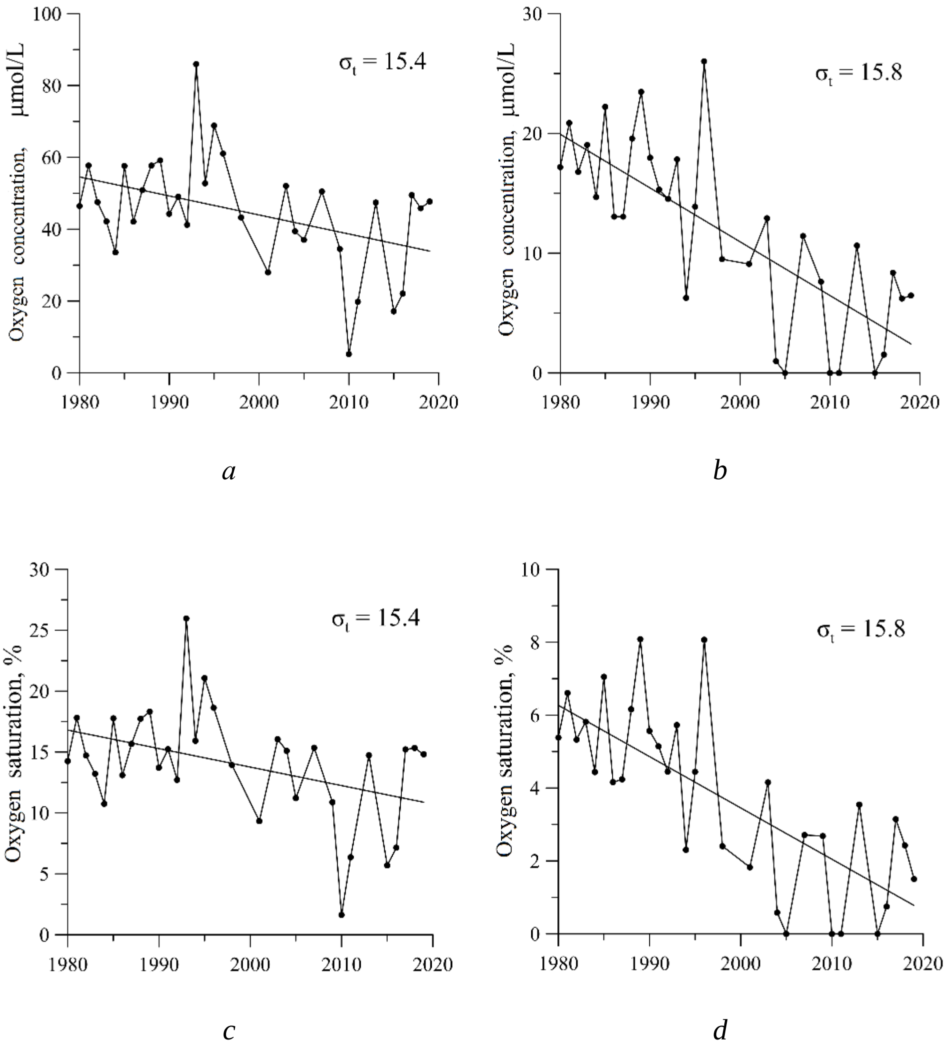


F i g. 7. Multi-annual changes in the oxygen concentration (*a*) and the degree of water saturation with oxygen (*b*) in the core of the CIL layer

That led to a decrease in the oxygen supply to deeper layers, both at the depth of the oxycline (σ_t = 15.4) and at the depth of the suboxic zone on-set (σ_t = 15.8) (Fig. 8).

A decrease in the oxygen concentration in the CIL led to a decrease in the oxygen gradient in the oxycline and, as a result, to a reduction in the physical flux of oxygen from the CIL to deep layers, which led to an upward shift in the upper boundary of the suboxic zone.

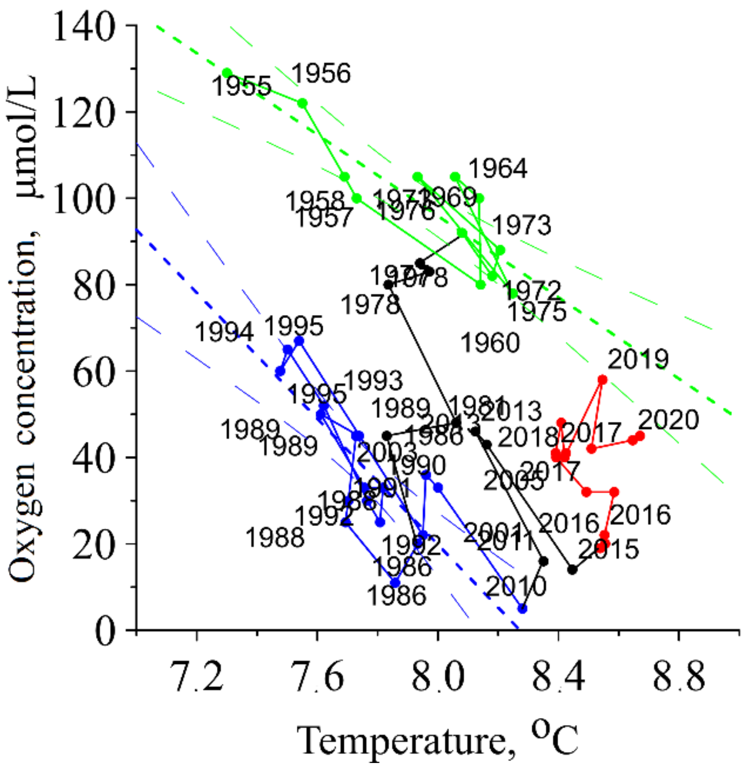
The oxygen supply in the main pycnocline was determined by the ratio of the oxygen flux from the CIL, due to ventilation in winter, and the rate of oxygen consumption for the organic matter oxidation, due to phytoplankton primary production. The dependence of the oxygen concentration on temperature was almost linear (Fig. 9), and the decrease in the oxygen supply in the second half of the 1980s – early 1990s indicated an increase in the flux of sinking particulate organic matter as a result of eutrophication since the temperature values during this period indicated intensive ventilation of waters [26].



F i g. 8. Multi-annual changes in the oxygen concentration (*a*, *b*) and water saturation with oxygen (*c*, *d*) in the oxycline layer (*a*, *c*) and in the suboxic zone (*b*, *d*)

The lowest oxygen content in the layer of the main pycnocline at high temperatures was in 2010, which indicated a decrease in ventilation intensity and reduction in the physical flux of oxygen from the upper layers (Fig. 9). However, there took place a gradual increase in the oxygen content in the middle part of the main pycnocline after 2010. The oxygen concentration increased from 5 µmol/L in 2010 to 45 µmol/L in 2020, despite the continued increase in temperature in this layer of seawater. Moreover, the data on the oxygen content indicated that the Black Sea approached in 2019–2020 the state before the eutrophication onset in the early 1970s.

It suggested that the dystrophication process ended in the Black Sea, eliminating the result of anthropogenic eutrophication, and that the oxygen dynamics in the sea waters is determined in the modern period by the intensity and dynamics of physical processes of water ventilation.



F i g. 9. *T*-O diagram of the Black Sea waters at the depth of the mid part of the main pycnocline (σ_t = 15.4) based on the multi-annual data

Conclusions

According to our data on the annual primary production value, a significant increase to 400 g C/m^2·year took place in the first half of the 1980s, then it decreased to an average of ~ 140 g C/m^2·year from 1985 to 1995, and, it remained at a level of ~ 100 g C/m^2·year after 1998.

Such variations in the primary production were in line with the observed changes in the vertical distribution of nitrate, as one of the main products of oxidation of sinking organic matter in the main pycnocline and oxycline layer. The maximum concentration of nitrate increased from 2–3 µmol/L in 1969 to 10–12 µmol/L in 1991 and then decreased to 2–3 µmol/L by now. That confirmed the fact of dystrophication, which practically eliminated the result of anthropogenic eutrophication of the Black Sea in the 1980s.

The revealed trend of increasing temperatures of the upper layers of the water column and a decrease in the intensity of winter convective mixing resulted in a decrease in the oxygen supply to all layers of the Black Sea aerobic zone. That led to the lowest oxygen content for the entire observation period in 2010.

At the same time, the process of dystrophication contributed to the return of the Black Sea system to its natural state, when the oxygen dynamics was determined mainly by the variability of the intensity of the physical ventilation of waters.

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