

Analysis of Observations and Methods of Calculating Oceanic Hydrophysical Fields

The distribution of oxygen and hydrogen sulfide in Black Sea waters during winter–spring period*

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Abstract — Regularities of oxygen and hydrogen sulfide are examined, using the method of spatial isopycnic analysis. The contribution that ventilation of winter-time surface waters over the domes of cyclonic gyres makes to the transfer of O_2 towards the upper boundary of the constant pycnocline and to the oxicleine layer is demonstrated. The paper provides spatial scales of this phenomenon and indicates the areas where the upper boundary of the anoxic layer in the Black Sea, relative to the conventional density, is located much higher compared with the rest of the sea. The suboxic zone is shown to be a specific feature of the O_2/H_2S distribution in the Black Sea waters, typical, at least, of the northern part of the basin. Analysis of the suboxic spatial variability in the vertical has been conducted.

INTRODUCTION

The starting point in the history of explorations of the specific features and O_2/H_2S vertical distribution in the Black Sea in ref. 1. By the 1920s, the study of the anoxic phenomenon in the Black Sea abyssal waters had become a regular practice. In the 1970s and early 1980s, only four institutions of the former USSR State Committee for Hydrometeorology annually conducted, at least, four expeditions, in the course of which most of the sea area or the larger part of it was covered by a network of stations. A number of leading research institutions of the country, namely, the Marine Hydrophysical Institute, the Institute of Biology of Southern Seas, Moscow State University, the Shirshov Institute of Oceanology being amongst them. As a result of the implementation of those works, by the end of the 1980s, a huge amount of data had been accumulated, but this still did not allow us to describe in fine detail the hydrochemical structure of the interface between the oxic and anoxic layers (80–250 m) and to study the processes determining its spatio-temporal variability [2, 3]. Another significant default hampering an efficient utilization of the *in situ* data were the methods of determination of the dissolved O_2/H_2S content, the imperfection of which gave rise to random and regular errors occurring in the course of measuring small concentrations of the elements being studied. For these reasons, it appears problematical to reliably predict variations of the anoxic boundary in the Black Sea, using the data collected prior to the mid-1980s [4–6].

In 1984–1985, the Marine Hydrophysical Institute, the Ukraine's National Academy of Sciences, initiated regular investigations of the chemical structure of the oxic/anoxic

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interface. The principal objective of these studies was to gain a deeper insight into the mechanism behind the spatial variability of the anoxic layer on diverse time scales. Amongst the achievements of these works, we consider (i) the increasing of the discreteness of sampling within the O_2/H_2S interaction layer up to 5 m and (ii) analysing of the latter layer's chemical structure. Furthermore, of overriding relevance are refs 7 and 8, which show that when standard methods are employed [9], seawater samples recovered in the vicinity of the H_2S layer prove to be oxidized; hence we have to cope with significant errors when monitoring the boundary of the anoxic zone, with the errors themselves attaining 10–15 and $3 \mu M l^{-1}$, for the oxygen and hydrogen sulfide, respectively.

The pioneering data obtained by the Soviet marine oceanographers indicated [10] that the C-layer, i.e. the O_2/H_2S co-existence layer, with the respective concentrations and thickness of the layer being $15\text{--}20 \mu M l^{-1}$ and 50–70 m, respectively, is an artifact resultant from the deficiency of the sampling techniques. It had also been found that in the samples taken from the co-existence layer, H_2S was not oxidized, with the exception of the uppermost part of the layer [11]. However, the relevant data were rather scarce, as the methods of protecting the sampled fluid from oxygenation were labour-consuming and were not always employed in the field conditions. It is in this context that the evolution of notions about the mechanisms and processes controlling O_2/H_2S spatial distribution, the C-layer parameters, and the depth of the anoxic layer in the Black Sea was examined in ref. 12.

Despite the fact that the initial evidence about the absence of a C-layer in the Black Sea were published as long ago as in 1984, following the investigations carried out in 1965 [13], the hypothesis was confirmed in the most convincing manner only in 1988 after the implementation of researches by the R/V *Knorr* [14]. Moreover, the investigators had pointed to both the lack of a C-layer and the presence of a suboxic zone where, in keeping with data in ref. 14, oxygen and hydrogen sulfide concentrations are 10 and $5 \mu M l^{-1}$, at most. At the same time, the improper consideration of the effect of hydrodynamic processes and specific features of hydrological structure of Black Sea waters, made in the course of interpreting the data compiled by the R/Vs *Knorr* and *Atlantis-II* in 1988 and 1969, respectively, had led the author of ref. 15 to a fallacious inference implying a steady rising of the anoxic boundary by 30 m in the central part of the western Black Sea in 1969 to 1988.

Analysis of the historical H_2S data collected in the Black Sea over the period from the 1920s to 1990s [16] had made it possible to show that synoptic, seasonal and inter-annual variations of the depth of the anoxic layer may attain 60 to 80 m in the vertical and, in large measure, are determined by the intensity of hydrodynamic processes. At the same time, no multi-annual unidirectional trend in the vacillations of the boundary of anoxic waters during that period had been revealed [16, 17]. In a number of papers published in recent years, one can find results of the statistic calculations, allowing an hypothesis that variations of the O_2/H_2S interface are oscillatory and occur on climatic scale [18].

References 3, 10–12, 16 and 17, in a definite sense, demonstrate the limited possibilities of the analysis of the variability of oxygen/hydrogen sulfide vertical distribution, using indices averaged over individual areas or the entire sea. Given such an approach, the O_2/H_2S variability over the water column is governed by the intensity of hydrodynamic processes facilitating the redistribution of the available stock of these substances. The identification and study of the actual variations of the O_2/H_2S content in various strata of the sea, relying on that analysis, seems hardly feasible.

The application of unidimensional isopycnic analysis to investigate the hydrochemical structure of the Black Sea [19–26] has made possible the demonstration of the relative universality of the vertical distribution of the basic parameters. Although specific features of the vertical distribution of chemical elements over the water column are observed at various depths and in diverse parts of the sea, they are linked with the same density layers of waters. In fact, the use of a scale of conventional density in place of the traditional depth scale allows us to separate the effect of various dynamic process upon the depth and configuration of isopycnic surfaces.

The unidimensional isopycnic analysis employed today assumes the absence or the equality of diapycnic fluxes of matter and intensity of diverse biochemical processes over the test area, leading to the redistribution of oxygen and hydrogen sulfide at specific isopycnic surfaces. As a result, the observed scatter of concentrations of individual hydrochemical parameters *versus* conventional density, particularly in the layers with extreme values, is accounted for by the imperfection and insufficient accuracy of the depth of the suboxic layer [15, 23]: apparently, the resultant spatial variations of the intensity of O_2/H_2S interaction, as well as the intra-annual transformation of the structure of the vertical hydrochemical parameter distribution in various parts of the Black Sea, along with the mechanisms responsible for those processes, have not been examined in the available published papers. Therefore the objective of the present work is to study the distribution of O_2 and H_2S in the Black Sea during the winter-spring-time period by treating *in situ* measurements data by the method of spatial isopycnic analysis.

MATERIAL AND METHODS

As original material for the study, we have used the data collected during Cruise 30 of the R/V *Professor Kolesnikov* from 2 to 30 April 1993. The arrangement of stations is shown in Fig. 1.

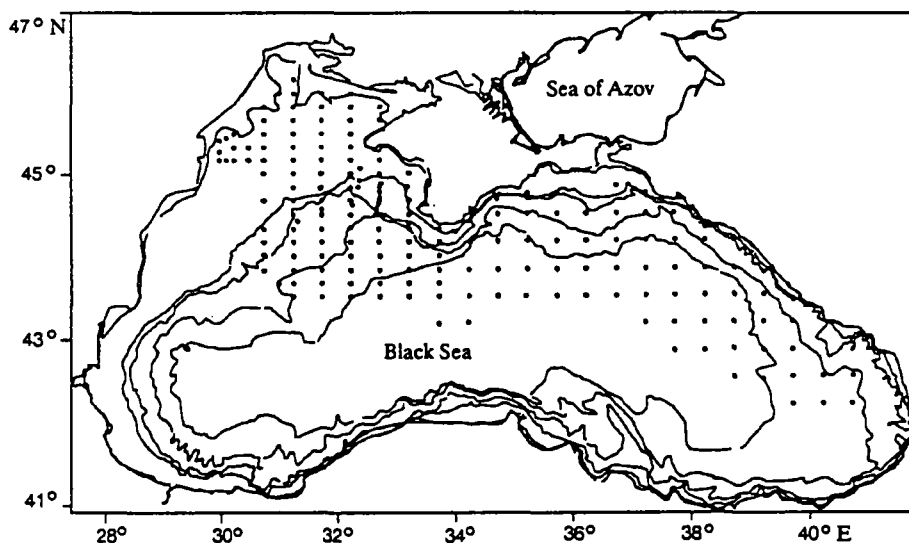


Figure 1. Schematic arrangement of the drift oceanographic stations occupied during Cruise 30 of the R/V *Professor Kolesnikov*.

Seawater was sampled using the probe ISTOK-7, featuring a rosette of 16 bathometers, the volume of each bottle being 1 litre. Particular emphasis was laid on the study of the vertical distribution of the principal hydrochemical parameters at the O_2/H_2S interaction zone. Sampling depths there were taken to coincide with the following isopycnic surfaces: 14.6, 14.8, 15.0, 15.2, 15.4, 15.6, 15.8, 15.9, 15.95, 16.0, 16.05, 16.10, 16.15, 16.20, 16.30, and 16.40 units of conventional density.

The concentrations of oxygen and hydrogen sulfide were determined immediately after they were sampled. Oxygen content was found by Carpenter's technique which was itself a modification of Winkler's method [27]. For analysis, we employed 100-ml narrow-necked glass flasks that were well blown through with dry air and filled with argon. Immediately after the retrieval of the rosette aboard the ship, the fluid from the bottle (50 to 100 ml) was poured into another vial. In calculating O_2 concentration, its content in the reagents used for fixing the samples was considered. The reproducibility of the analysis was $1 \mu M l^{-1}$, and the possible contamination of samples with oxygen did not exceed $2 \mu M l^{-1}$. Hydrogen sulfide content was determined by the iodometric method in conformity with ref. 27. The iodine/hyposulphite ratio was derived for the depth layers situated 5–15 m above the upper boundary of the anoxic zone.

ANALYSIS OF DATA

Figure 2 shows distribution of oxygen and hydrogen sulfide *versus* relative density, derived from the observations carried out during Cruise 30 of the R/V *Professor Kolesnikov*. In general, vertical distribution of the sampled elements differs little from the distributions submitted in refs 21, 24 and 25. As in the previous works, for any individual value of conventional density, we observed that O_2 concentrations changed within definite bounds; however, in the case being studied, the range of the concentration's variability was much larger and exceeded the possible error of determination. Three layers displaying the characteristic vertical oxygen distribution were singled out: (i) between the sea surface and the isopycnic surface, the relatively close values of oxygen content were observed; (ii) from 14.5 to 15.6–15.9, oxygen concentration decreased from 300–350 to $10 \mu M l^{-1}$; and (iii) at the depth levels, with conventional density above 15.9; and down to the depth of the anoxic layer ($\sigma_t \sim 16.2$), at all deep-water stations, an area labeled suboxic was observed [23].

Although the vertical oxygen distribution's was roughly the same, with the conventional densities observed in April 1993 and July 1992 (Cruise 29 of the R/V *Professor Kolesnikov*) being the same, O_2 concentration in April 1993 was larger. The growth of O_2 concentration from July 1992 to April 1993 was as follows: about $40 \mu M l^{-1}$, with $\sigma_t = 14.5$; about $90 \mu M l^{-1}$, with $\sigma_t = 15.0$; about $50 \mu M l^{-1}$, with $\sigma_t = 15.2$; and $20 \mu M l^{-1}$, with $\sigma_t = 15.5$. These values depict the inter-annual oxygen content in separate layers of the Black Sea.

Figure 3a shows the depth of the upper boundary of the anoxic layer in the Black Sea. It varied from 88 to 220 m, which is consistent with the range of values documented during the previous field researches. Naturally, the smallest values were observed in the areas where central cyclonic features occurred, and the smallest values were recorded within anticyclonic vortices in the vicinity of the continental slope (Fig. 3a). During the expedition, we repeatedly revealed analytically significant O_2 concentrations at the depth of the anoxic layer, the largest being $6 \mu M l^{-1}$. On the other hand, we did not find, at least, two adjoining depth levels where concentrations of oxygen and hydrogen sulfide

would be larger than $2-3 \mu M l^{-1}$. Considering the possible degree of contamination of samples by the air oxygen (up to $2 \mu M l^{-1}$), it may be assumed that even if the O_2/H_2S co-existence layer, with concentrations of $1-2 \mu M l^{-1}$, does occur, its thickness does not exceed 0.1 conv. unit, or 5–10 m.

The beginning of the hydrological spring, during which field investigations were being conducted, is characterized by the high level of aeration of waters (sea surface temperature in the deep-water part of the sea and in the north-western shelf area was 8–9 and 4–8°C, respectively), whence ensues that observations of a C-layer, significant in terms of thickness and concentration, are rare and command a special study. However, it should be admitted that the presence of the C-layer that has been broadly debated in oceanographic literature, mostly was an artifact resultant from the application of an imperfect methodology of determination of O_2 concentration, which yields overstated values in the O_2/H_2S transitional.

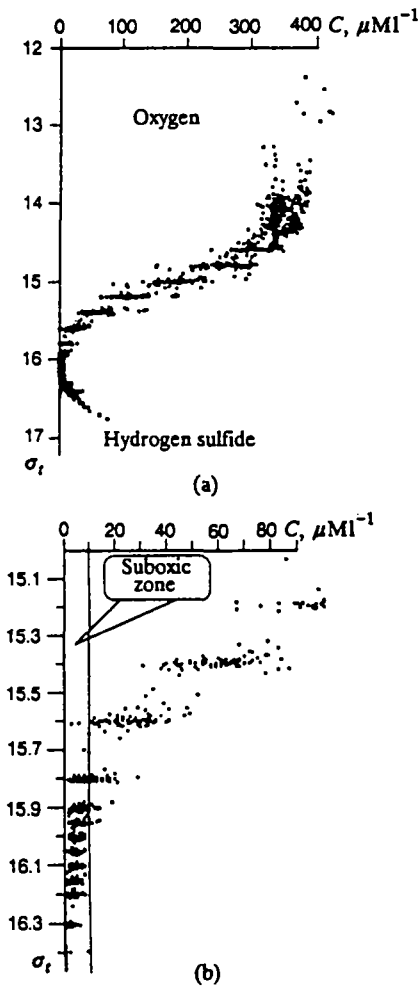


Figure 2. Oxygen and hydrogen sulfide distribution versus (a) relative density and (b) oxygen on magnified scale for the whole of the data.

HYDROGEN SULFIDE

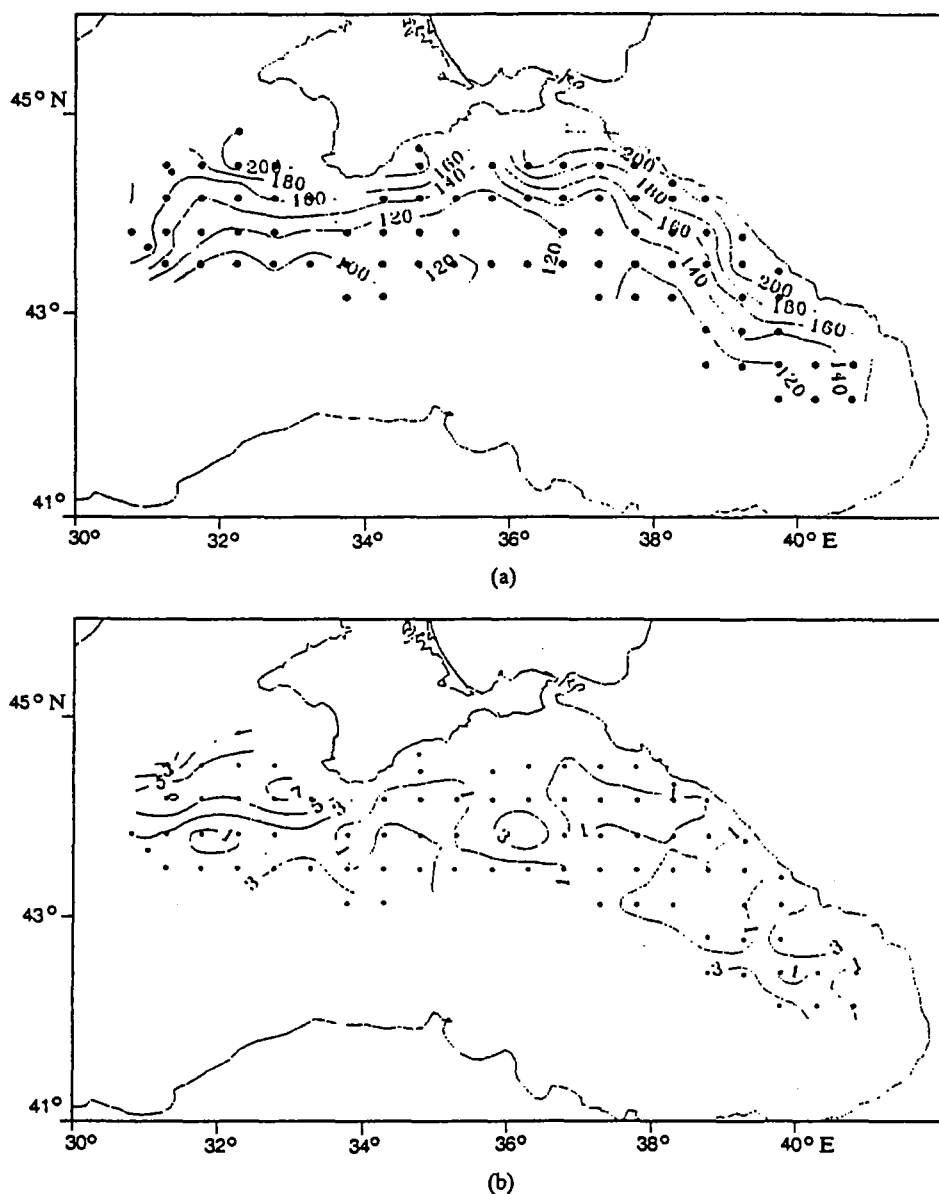


Figure 3. (a) The depth (m) of the sulfide contour $3 \mu\text{M l}^{-1}$ and (b) the distribution of H_2S ($\mu\text{M l}^{-1}$) at the 16.20 isopycnal surface.

The distribution of hydrogen sulfide over the isopycnal surface 16.2 is shown in Fig. 3b. The isopycnal surface given, for most of the studied area, represented an upper boundary of the anoxic zone ($1 \mu\text{M l}^{-1}$) in the Black Sea in April 1993. The mean value of 16.24 for the conventional density of the sulfide contour $3 \mu\text{M l}^{-1}$ (which is, analytically, more

authentic compared with the sulfide contour $1 \mu M l^{-1}$) was calculated for the entire set of observations carried out during Cruise 30 of the R/V *Professor Kolesnikov*. This values agrees well with the similar values submitted in refs 12 and 20–23.

At the same time, the data given allow us to discuss the issue of some definite geographic regularity in the position of sulfide contours in the density field. Figure 3b shows that alongside some minor values ($0-3 \mu M l^{-1}$), for the larger part of the Black Sea, there is an area south-west of the Crimea that displays large H_2S concentrations. The distribution of the H_2S concentration over the isopycnic surface 16.2 does not allow us to unambiguously determine its relationship with hydrodynamic processes. The location of the area with high hydrogen sulfide concentration near the continental slope edge (Fig. 3b) allows only the suggestion that peculiarity in the distribution of hydrogen sulfide is coupled with the interaction of NW shelf waters from the abyssal sea. This interaction, specifically, may manifest itself through an enhanced influx of particulate organic matter (POM) produced in the NW shelf waters or discharged by the rivers. It is clear that the larger amount of sediments will lead to the intensification of all biochemical processes, including those of sulphate reduction. It will be natural to suppose that some areas accumulate larger quantities of POM: hence, H_2S is being produced there more intensively. Such areas are supposedly situated near Rumania's and Bulgaria's continental slope, as a considerable amount of POM of both allochthonous origin and autochthonous origin area is transported to those areas; and one more area is expected to occur in the central basin, following the winter-spring-time phytoplankton blooming. However, these hypotheses must be experimentally supported.

The growth of H_2S concentration revealed at the isopycnic surface 16.2, in contrast to synoptic oscillations of the boundary of anoxic waters, reflects the actual variations of H_2S content in some local parcels of water. The area of continental slope must be intensively studied, because it is there that the major sources of hydrogen sulfide seem to be located, which are responsible for the growth of H_2S concentration in some layers of water.

Thus the method of spatial isopycnic analysis permits those areas to be identified where active chemical/biological processes are underway, and shows that H_2S spatial distribution is not strictly isopycnic. Hence, from the viewpoint of the estimation of physical/chemical dynamics of the anoxic zone, there is no reason to seek some 'universal' value of the physical indicator for determining the border of anoxic waters.

OXYGEN

Oxygen distribution at some isopycnic surfaces is shown in Fig. 4. First of all, it should be noted that geographic regularities in the O_2 distribution are traceable there, which may account for the range of concentrations occurring at the individual values of conventional density (Fig. 2). This facilitates not only the description of regularities in the spatial variability of the O_2 vertical distribution within individual fluid layers but also the identification of the most relevant processes contributing to their formation.

As the investigations were conducted at the beginning of the spring hydrological season, the distribution of the hydrochemical indices, specifically, oxygen, portrayed the ultimate winter-time ventilation of water. According to refs 28–31, winter-time ventilation in the central basin impacted by the major cyclonic gyres encompasses seawater layers having the higher density, in comparison with other areas of the sea. This inference is supported by the Fig. 4a data: maximal O_2 concentrations for the entire northern

Black Sea at the isopycnic surface 14.6, characteristic of the upper part of the constant pycnocline and oxcline, were observed in the western section of the basin where cyclonic gyres had reached a peak in their evolution. Such a distribution of oxygen allows a deduction that during the winter of 1992–1993, surface water ventilation in those areas of the sea was most intensive. The deduction is confirmed by the results of the study on variability of the nitrate/phosphate vertical structure during the expedition [32]. The phosphate vertical distribution underwent a substantial transformation *versus* conventional density up to $\sigma_t = 15.6$ –15.7.

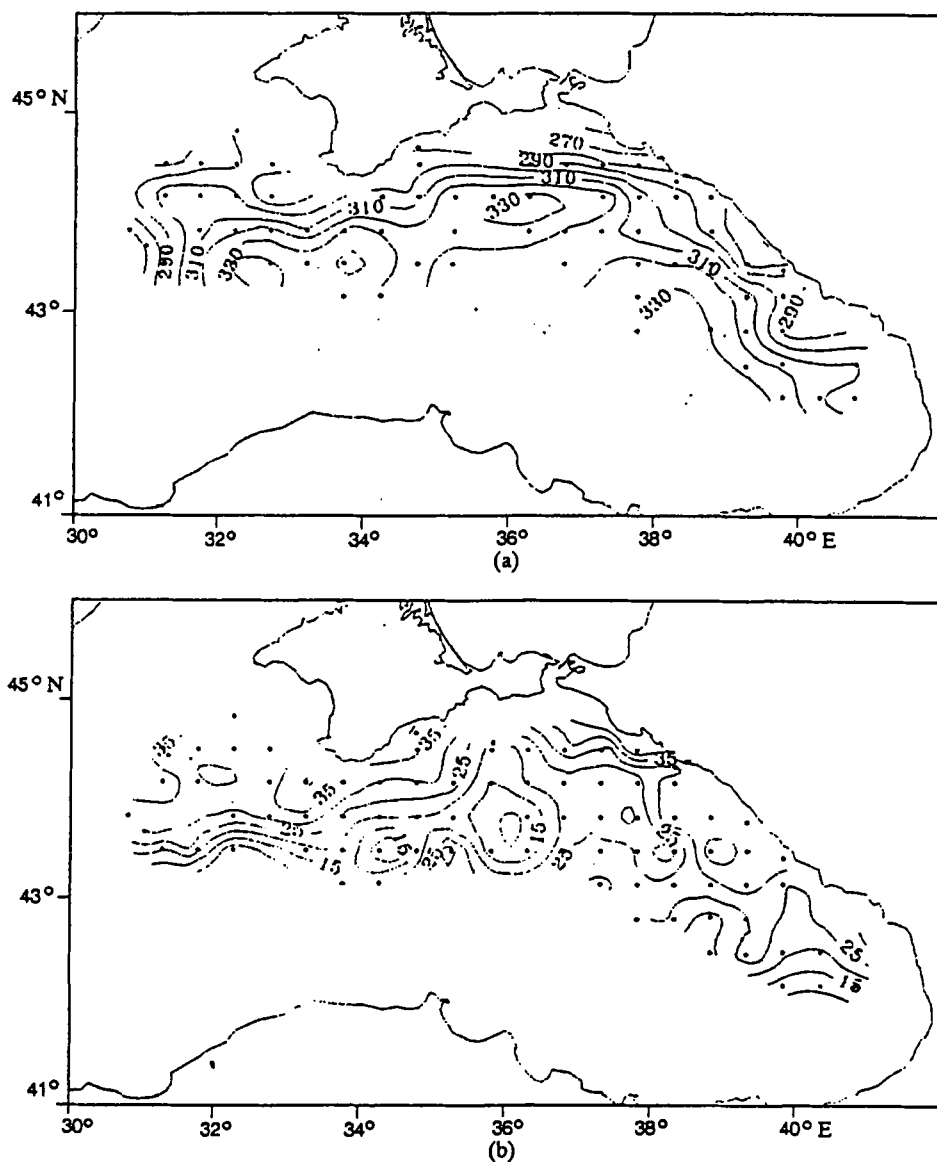


Figure 4. Oxygen distribution ($\mu\text{M l}^{-1}$) at the isopycnic surfaces (a) 14.60 and (b) 15.60.

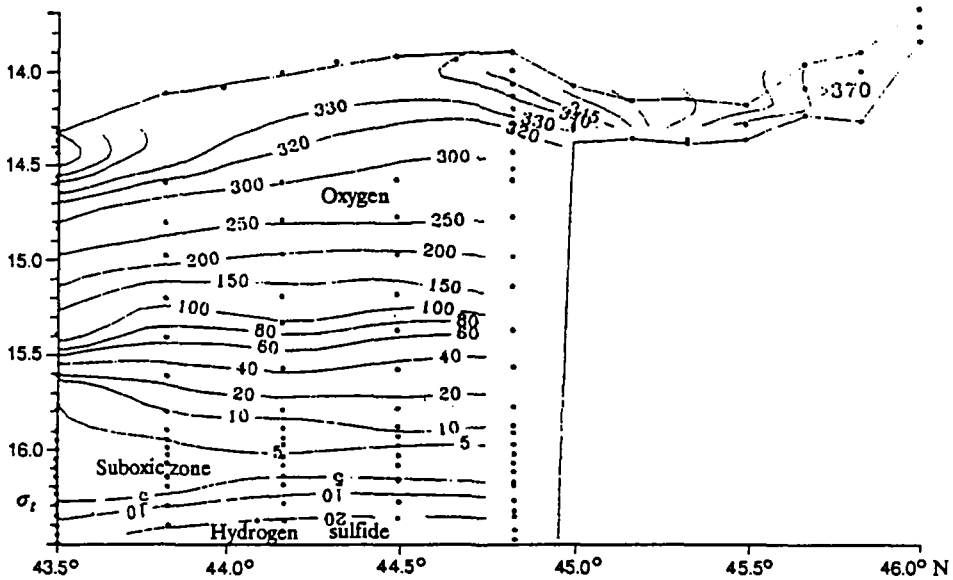


Figure 5. Oxygen and hydrogen sulfide distribution ($\mu M l^{-1}$) versus relative density at the transect made along $32.25^\circ E$.

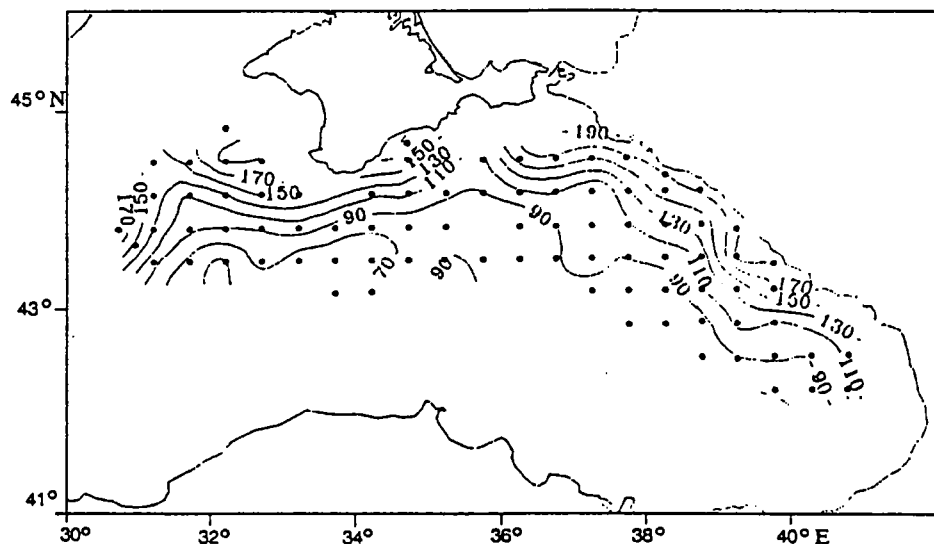
Oxygen distribution at the isopycnic surface 15.6 (Fig. 4b) that corresponds to the lower part of the oxicleine, fundamentally differs from that considered above (Fig. 4a). Starting from conventional density ~ 15.5 – 15.6 (Figs 4b and 5), O_2 vertical distribution exhibits smaller concentrations in the central part of the sea, and larger concentrations in the margins of the abyssal area. Analysis of the O_2 distribution at the transect made along $32.25^\circ E$ (Fig. 5) demonstrates that at the southernmost station, occupied in the area strongly impacted by the western cyclonic gyre, oxygen content contours deviate towards the larger values of conventional density up to $\sigma_t \sim 15.5$. At the same time, for the waters with $\sigma_t \sim 15.5$, the deflection of oxygen content contours to the inverse direction is characteristic. That process is so strongly pronounced that, at $\sigma_t \approx 15.6$, oxygen concentration is reduced to $10 \mu M l^{-1}$, i.e. to the value characteristic of the upper border of the anoxic zone. That distribution is indicative not only of the vigorous ventilation processes whereby O_2 is supplied to the main pycnocline layers in the areas of cyclonic gyres, but also of the intensive processes in which oxygen participates (such as oxidation of the organic matter and other reduced compounds, and denitrification) in the vicinity of the anoxic layer, i.e. the suboxic zone.

SUBOXIC ZONE

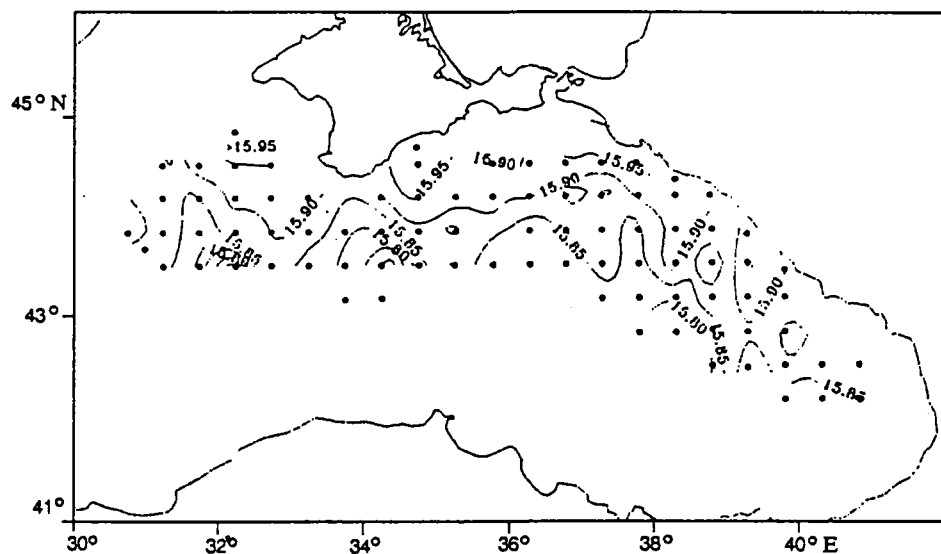
The data acquired during Cruise 30 of the R/V *Professor Kolesnikov* point to the availability of a suboxic zone (i.e. a layer of water with oxygen and hydrogen sulfide concentrations of 10 and $3 \mu M l^{-1}$, respectively) over the entire northern half of the deep-water Black Sea, which confirms the inferences made in refs 23 and 26.

Figure 2b shows the vertical distribution of oxygen with the range of conventional densities 15.0 – 16.5 . Contour $10 \mu M l^{-1}$ in the studied part of the sea (Fig. 6a) was consistent with the location and intensity of various dynamics features. The least depth (45 m) is characteristic of the cores of cyclonic gyres, and the largest depth (197 m) coincided

with the location of the major cyclonic gyres in the vicinity of the continental slope edge. The acquired results are rather trivial, as the development of cyclonic gyres leads to the rising of isopycnic surfaces, and the evolution of anticyclonic vorticity results in the descending of isopycnic surfaces.



(a)



(b)

Figure 6. The depth of (a) the upper boundary of the suboxic zone (oxygen concentration contour $10 \mu\text{M l}^{-1}$) (b) conventional density (conv. units).

Somewhat unexpected was the spatial variability of the upper boundary of the suboxic zone *versus* relative density (Fig. 6b). It is seen that minimal values of the conventional density occurred in the central basin, with the smallest value (15.61) having been observed within the western cyclonic gyre.

The winter-time convective ventilation accompanied by the sinking of cool oxygenated surface waters is most intensive above cyclonic gyres in the central sea [28, 31]. This would be expected to lead to the influx of oxygen to the layers in the central sea containing dense fluid, compared with the coastal zone. The actual picture, at $\sigma_t > 15.5$, is opposite to the anticipated one and is rationalized by the fact that not only is there a powerful oxygen flux to the dense layers in the central sea areas, but also, it is depleted in the course of the oxidation processes.

The thickness of the suboxic zone alters from 0.6 units of conventional density at the centre of the western cyclonic gyre to 0.2 unit (14 m) in the vicinity of the continental slope (Fig. 7). The build-up of thickness of the suboxic zone in the core of cyclonic gyres saliently stands out with respect to both the scale of relative density and the depth scale. The latter point would be at bias with the notorious dependence of the thickness of density layers upon the vertical stratification of waters, if the configuration of the suboxic zone boundaries were isopycnic. In conformity with the peculiarities of the spatial variability of vertical stratification of Black Sea waters, the thickness of the layer bounded by two isopycnic surfaces is expected to become larger from the centre of the deep-water part of the sea to its periphery. However, the position of the suboxic zone's boundaries, particularly, of the oxygen content contour $10 \mu M l^{-1}$, is essentially non-isopycnic. This allows an assumption that it is in the central sea that active chemical processes responsible for the generation of the zone at issue are taking place. If the formation of the suboxic zone is directly linked with oxidation-reduction reactions at the oxic/anoxic interface, then further study of the formation of the suboxic zone appears to be of the utmost importance for gaining insight into the dynamics of H_2S content and propagation in the Black Sea.

We can trace the variation of the depth of the suboxic zone in the conventional density field shown in Fig. 5. The sharp and considerable increase of the suboxic layer's thickness takes place near the southernmost station of the transect. Over a distance of 20 miles, its values alter nearly two-fold, with the layer's depth basically increasing near the central sea areas due to the rising of the oxygen content contour $10 \mu M l^{-1}$, whereas even if sulfide contours deepen, that deepening is weakly exhibited. At the same time, the presence of a powerful quasi-stationary anticyclonic eddy at $32.25^\circ E$, $44.50^\circ N$ affects but slightly the isopycnic O_2 and H_2S distribution, or the thickness of the suboxic zone (Fig. 5). A similar picture was observed in the case of the vertical distribution of biogenic elements [32]. All this allows a supposition that in the course of the evolution of an anticyclonic eddy south-west of the Crimea in April 1993, only isopycnic transport took place, whereas the intensity of diapycnic fluxes of matter did not change.

The acquired range of the suboxic layer's variability (14–51 m) virtually coincides with the range submitted in ref. 15, relying on the data compiled by the R/V *Knorr* in May–June 1988. Bearing in mind that the expeditions were carried out in different hydrological seasons, including winter, when ventilation above the upper part of the main pycnocline is most pronounced, we can support the inference [26] that the suboxic layer with the inherent characteristics describe above represents the basic peculiarity of the chemical structure of Black Sea waters.

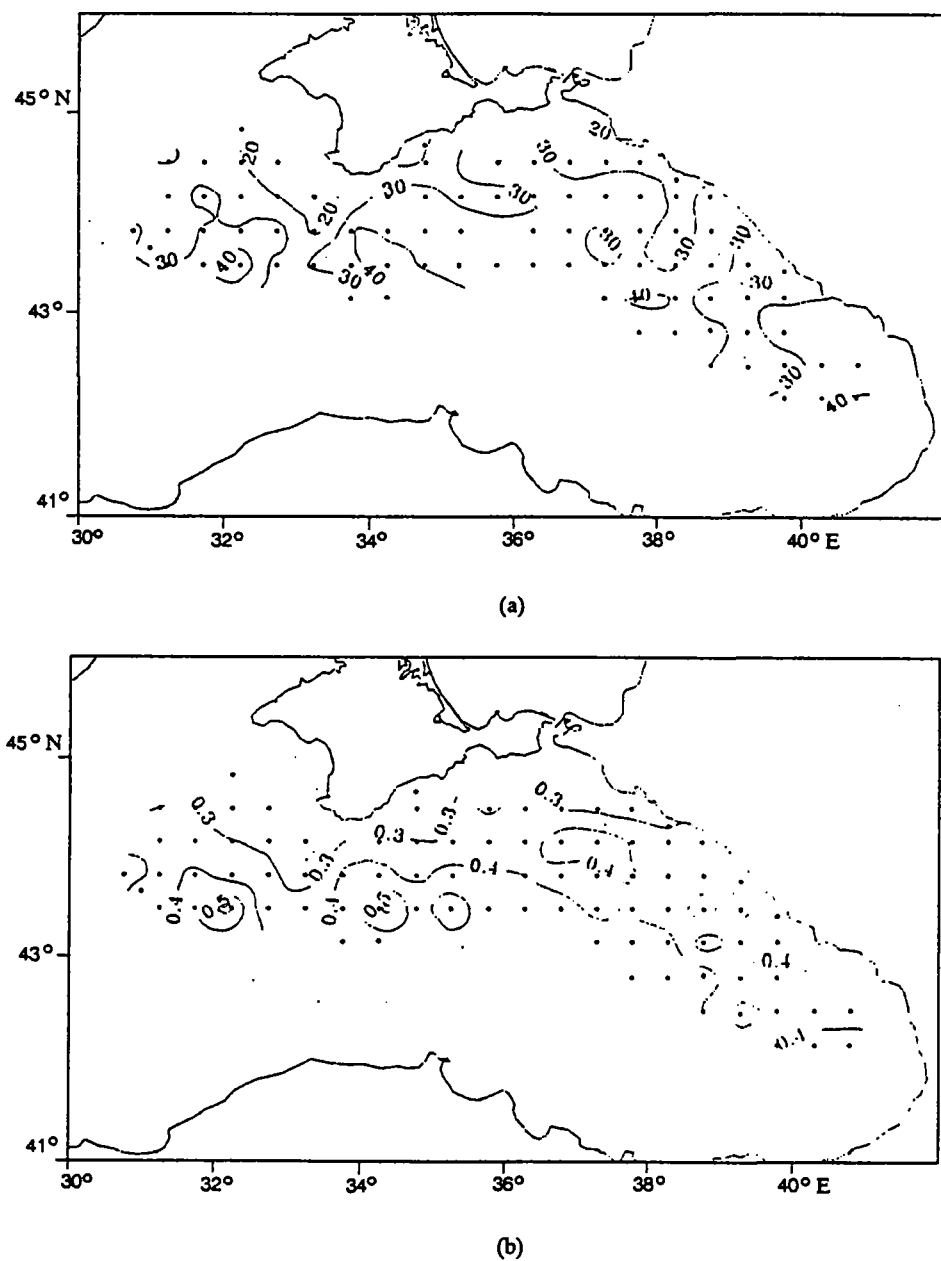


Figure 7. Thickness of the suboxic zone given in (a) metres and (b) conventional units.

Acknowledgements

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