Features of the Oxygen and Sulfide Vertical Distribution in the Black Sea Based on the Expedition Data Obtained by Marine Hydrophysical Institute in 1995–2015

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Discussed are the features of the oxygen and sulfide vertical distribution resulted from the expedition data obtained by Marine Hydrophysical Institute in the northern part of the Black Sea (within the economic zone of Russia) in 1995–2015. In course of the last 20 years, the upper boundary of the sulfide zone in this area, defined by the sulfide isoline 3 μM, did not change its position in the scale of relative density and is located on σ_t = 16.10–16.15 kg/m^3. Closer to the northwest shelf (in the area of the Sevastopol anticyclone), the hydrogen sulfide isoline 3 μM is slightly lifted to σ_t = 15.9–16.0 kg/m^3; there is a single case when its position was recorded at σ_t = 15.85 kg/m^3. Position of the suboxic zone upper boundary (the threshold oxygen isoline 10 μM) is characterized by spatial and temporal variability. During four expeditions in 2009–2013, in the region of the northwestern shelf the suboxic zone upper boundary was located, regardless of the season, within σ_t = 15.6–15.7 kg/m^3. In November, 2013 in the deep sea part, the threshold oxygen isoline 10 μM was located on σ_t = 15.7 kg/m^3, whereas in November, 2015 it was considerably higher: on σ_t = 15.35 kg/m^3. The change of location of the threshold oxygen isoline 10 μM observed in 1995–2015 provides no possibility to assess unambiguously alteration of the suboxic zone thickness in the central part of the sea. Thus within the depths 1750–2000 m in the Black Sea, no significant increase of the sulfide content in 1995–2015 has been recorded.

Keywords: oxygen, sulfide, suboxic zone, hydrogen sulfide zone, Black Sea.

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Introduction

Location of the sulfide zone in the Black Sea was systematically studied by the Soviet and, later, Russian oceanologists in the 1970s–1990s. In the 90s, comprehensive analysis of the obtained results gradually brought to development and application of the relative density σ_t-scale in order to make the data interpretation more logical and simple [1–12].

Since the early 90s, large-scale expeditions in the Black Sea covering the area from the Danube mouth to the Caucasian coast transformed into the studies of individual countries within their economic zones. For Marine Hydrophysical Institute (MHI), the 33rd cruise of the R/V "Professor Kolesnikov" in spring, 1995 became the final many-sided expedition in the Black Sea. Its results were discussed in the preprint [13]. The next complex expedition in the Black Sea (numerous group of the MHI scientists took part in it) was a cruise of the Bulgarian R/V "Akademik" in the region of the Sevastopol anticyclone in May, 2004. The obtained data analyzed the location of the upper and lower boundaries of the suboxic zone (the lower boundary of this zone is the upper boundary of the sulfide zone) above the continental slope [14].

The subsequent MHI expeditionary investigations were of a shortterm occasional character. The main area of researches reduced up to the northwestern shelf (NWS) of the Black Sea [15–17]. In the deep-sea part, the continental slope in the region of the Sevastopol anticyclone was studied rather constantly.

Reunification of Russia and Crimea, and the institute's transfer to the Russian Academy of Sciences started a new stage of expeditionary researches of MHI. In autumn, 2015 a joint expedition of MHI and the Institute of Oceanology (Moscow) was run in the region of the "century" section Cape Chersonese – Bosporus Strait. The expeditionary research in the deep-sea area along the Crimea coast and within the economic zone of Russia was planned for 2016–2017. Elaboration of a strategy for subsequent hydrochemical studies in the Black Sea laid down in MHI requires systematization of separate incomplete results obtained by the institute scientists after 2004. They are planned to be subsequently compared with the data that will be gotten from the future studies of the suboxic and sulfide zones. The present paper deals with this problem.

Materials and methods

The scheme of the MHI hydrochemical stations during the cruises in 2009–2015 is shown in Fig. 1. Sampling for chemical analysis was done using a 12-bottle cassette of a CTD-probe (produced by Sea-Bird Electronics, Inc.) at the depth of certain isopycnic surfaces. As a rule, the samples for sulfide were taken at the maximum depth and then along the σ_t = 16.30; 16.20; 16.15; 16.10; 16.05; 16.00; 15.90; 15.80; 15.60; 15.40 and 15.20 kg/m^3, which covered the suboxic zone completely. At the utmost southwestern station on the section Cape Chersonese – Bosporus Strait, the samples for sulfide were taken at 28 horizons: slightly less than 2000 m, then in every 100 m and, finally, at the σ_t cited above.

Such sampling permitted to define location of the upper boundaries of the intermediate suboxic layer and the sulfide zone, as well as the suboxic layer thickness, resolution is up to $\Delta\sigma_t$ = 0.05. It corresponds to the accuracy equal approximately to 5 m, according to the depth scale.

The sulfide content was defined by the iodometric method assuming that iodine consumption on the σ_t = 15.8 kg/m^3 is equal to zero and the oxygen concentration – by the Winkler method modified for sampling with low oxygen content according to the method [18]. In both cases, 15 minutes before sampling, the 200 ml volumetric flasks for fixing sulfide and the oxygen bottles with a narrow neck were flushed with argon.

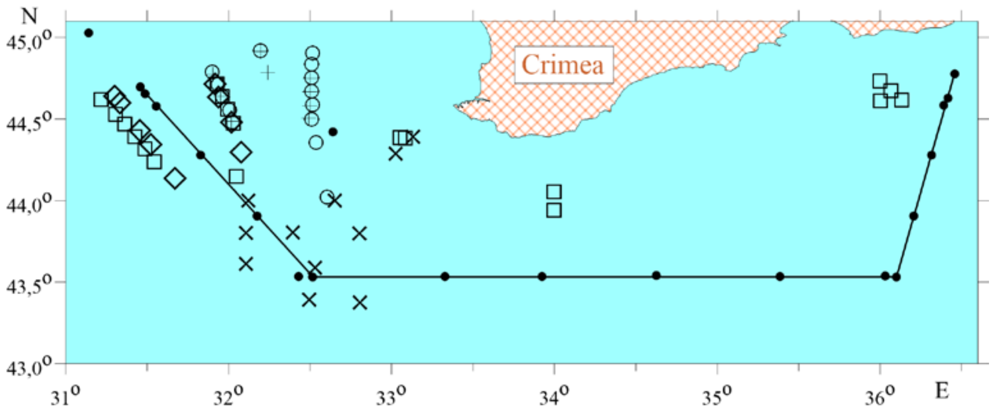


Fig. 1. Scheme of the stations where the H_2S and O_2 vertical profiles were done: + is R/V "Sapfir", May, 2009; ◊ is R/V "Professor Vodyanitsky", October, 2010; □ is R/V "Professor Vodyanitsky", August, 2011; o is R/V "Professor Vodyanitsky", September, 2013; ● is R/V "Maria S. Merian", November, 2013; × is R/V "Professor Vodyanitsky", November, 2015. Solid line marks the section carried out in November, 2013

Discussion of the results

The relatively detailed studies of the R/V "Akademik" in the region of the quasi-stationary Sevastopol anticyclone in 2004 showed that in the areas of the shelf transformation to the continental slope, the sulfide isoline 3 μM was located on the σ_t = 15.88 kg/m^3, whereas in the deep sea region the same sulfide concentrations were observed on the σ_t = 16.05 kg/m^3 [14]. Thus, it seems logical to consider individually the vertical profiles of oxygen and sulfide obtained in the region of the Sevastopol anticyclone continental slope in 2009–2013 and those obtained in the central deep-sea part in 2013–2015 and shown in Fig. 2, 3, respectively.

First of all, Fig. 2 demonstrates a good coincidence of configurations of the sulfide content data resulted from different surveys. That, in fact, permits to analyze all the data. The results obtained in May, 2009 do not fall into the pattern as they show that the sulfide concentrations within the interval σ_t = 16.0–16.4 kg/m^3 in the region of the continental slope at the NWS edge were slightly higher than those observed in all the other regions. This fact confirms the conclusion [14] that the sulfide isolines at the beginning of the continental slope go up to the higher σ_t, but it requires more scrupulous studies. In particular, it seems reasonable to include several stations where the depths correspond to the σ_t location near 16.1–16.2 kg/m^3 (approximately at 150–170 m) in the subsequent investigations of the vertical structures of dissolved oxygen and sulfide. The sampling interval should be $\Delta\sigma_t$ = 0.05 kg/m^3 up to the σ_t = 15.7 kg/m^3.

Fig. 3 provides a more detailed pattern of the oxygen and sulfide vertical distribution between the σ_t = 15.0–16.3 kg/m^3 where the suboxic zone is located; its upper boundary coincides with the oxygen isoline 10 μM (in some papers – 20 μM), and the lower one – with the sulfide isoline 3 μM (in some papers – 5 μM).

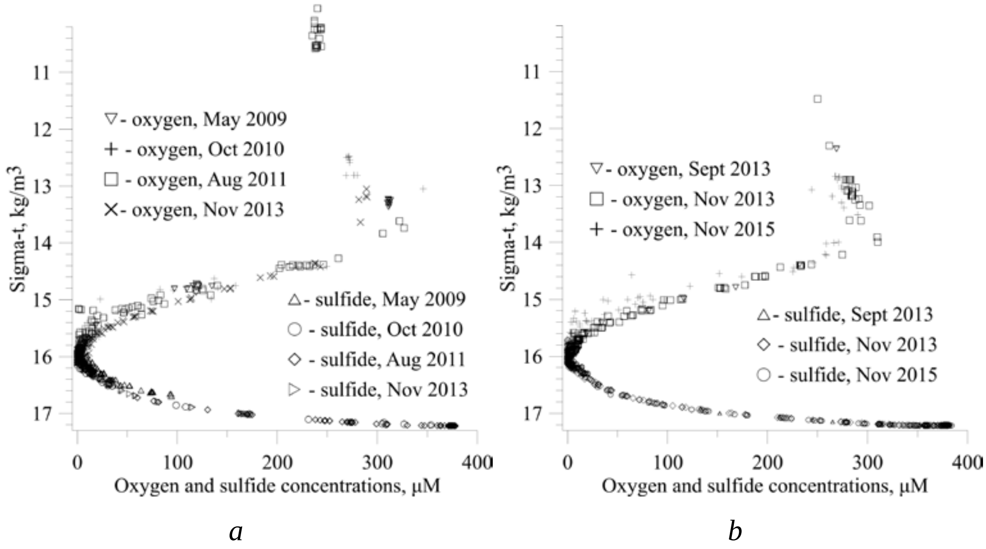


Fig. 2. Vertical profiles of oxygen and sulfide in the region of the Sevastopol anticyclone in 2009–2013 (*a*) and in the deep part of the Black Sea in 2013–2015 (*b*)

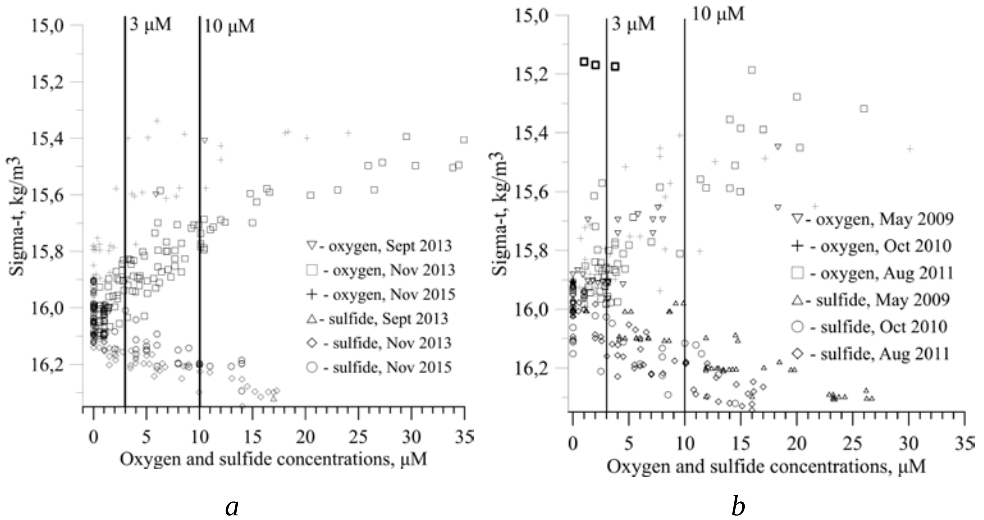


Fig. 3. Vertical profiles of oxygen and sulfide in the region of the Sevastopol anticyclone in 2009–2011 (*a*) and in the deep part of the Black Sea in 2013–2015 (*b*)

Fig. 3, *a* shows that in August, 2011, at the most western station, located at the beginning of the continental slope on the depth ~ 120 m (see Fig. 1), an almost zero oxygen content was recorded at the σ_t = 15.2 kg/m^3. This corresponds to the highest location of the suboxic zone upper boundary revealed in course of the studies.

Except for the already above-mentioned increased sulfide concentrations observed in May, 2009, Fig. 3 also shows that the oxygen concentrations exceeding 10 µM were recorded above the shelf edge at the σ_t = 15.7 kg/m^3 only in November, 2013, whereas in the deep-sea part such values were observed regularly. As for the $\sigma_t \geq 15.8$ kg/m^3, the oxygen content at them was lower than 10 µM in all the performed surveys.

The suboxic zone configuration and dimensions can be defined more accurately by the oxygen and sulfide vertical distributions at single sections. Thus, as for the Sevastopol anticyclone region, distribution of these elements on the sections perpendicular to the shelf edge in 2009–2011 is represented in Fig. 4. In May, 2009, on two sections, the sulfide isoline 3 µM was located above the σ_t = = 16.0 kg/m^3 rising (in the maximum case) up to σ_t = 15.85 kg/m^3 (Fig. 4, *a*). These data coincide with the results of the studies carried out from board the R/V "Akademik" in May, 2004 [14].

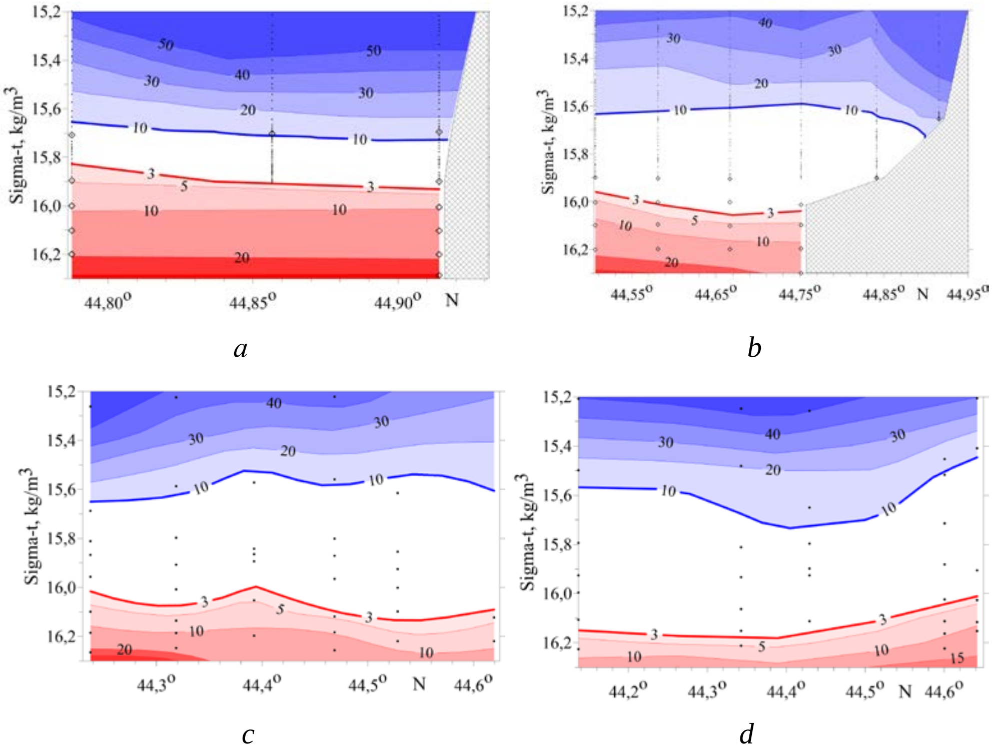
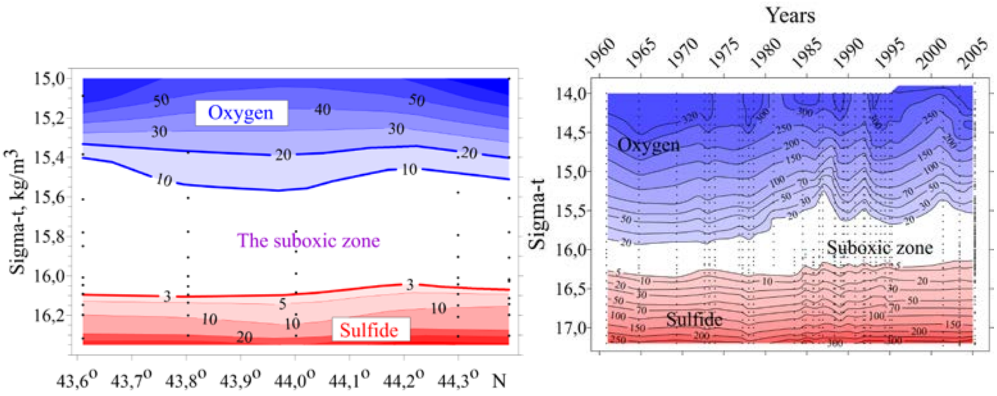


Fig. 4. Vertical distribution of the oxygen and sulfide concentrations, µM, on the Sevastopol anticyclone sections in May, 2009 (the meridian 32° E (*a*), the meridian 32.5° E (*b*)), August, 2011 (*c*) and October, 2010 (*d*); ◊ and ● denote the horizons of sampling

Most likely, the above noted sulfide isoline elevation (in the density scale) represents a seasonal phenomenon since in the very same region in summer, 2011 the sulfide isoline 3 µM was located below the σ_t = 16.0 kg/m^3, and in autumn, 2010 – just a little lower than the σ_t = 16.1 kg/m^3. In other words, during transition from spring to autumn, the gradual deepening of the sulfide isoline 3 µM is observed. However, one cannot exclude influence of water dynamics (for example, various phases of the Sevastopol anticyclone development [19–21]) on location of the upper boundary of the sulfide zone in this region.

On three sections the upper boundary of the suboxic zone (oxygen isoline 10 μM) was located approximately at the σ_t = 15.6 kg/m^3 (Fig. 4, *a*). Fig. 4, *a*, *b* shows increase of the oxygen content in the northern part of the sections above the continental slope. This feature of the oxygen distribution was revealed due to application of the oxygen sensor, which determined oxygen concentration with the resolution 0.5 m. But after 2009 it was not used that resulted in rougher and less reliable distributions.

In November, 2015 the "century" section Cape Chersonese – Bosporus Strait in the central part of the Black Sea was investigated. The parameters of its suboxic zone can be compared with the long-term data [6] (Fig. 5).



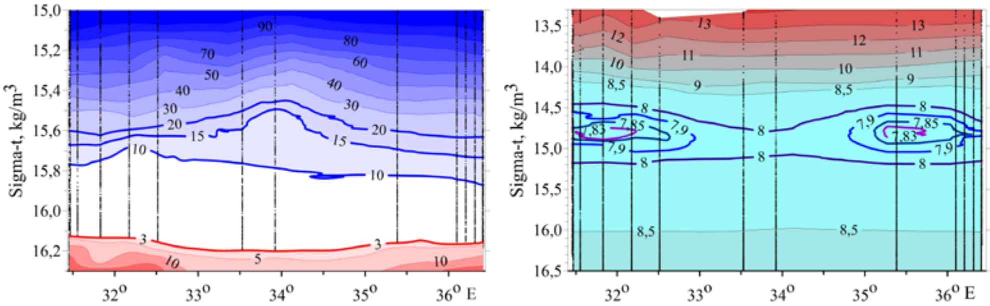
a *b*

Fig. 5. Vertical distribution of the oxygen and sulfide concentrations, μM, on the "century" section Cape Chersonese – Bosporus Strait in 2015 (*a*) and the one based on the multi-year data [6] (*b*)

Fig. 5 shows that in 2015 the lower boundary of the suboxic zone, i.e. the sulfide isoline 3 μM, was within the σ_t = 16.10–16.15 kg/m^3 (the distance between them, according to the depth scale, is about 5 m). The same position of 3 μM sulfide isoline was observed on the long-term data given in [6] (Fig. 5). According to the scientific literature data, the approximately same position of the sulfide isoline 3 μM was observed to the east and west off the "century" section Cape Chersonese – Bosporus Strait: in the northwest – at σ_t = 16.12–16.15 kg/m^3, in the southeast – at σ_t = 16.10–16.20 kg/m^3 [22–24]. Such long-term and spatial stability of location of the suboxic zone lower boundary is explained by sulfide oxidation due to the oxygen-containing Marmara Sea water inflow through the Bosporus Strait, whereas the vertical oxygen flow provides oxidation only of ~ 5 % of sulfide rising from the sea depth [10].

As for location of the suboxic zone upper boundary, it is characterized by temporal variability. This is confirmed both by the long-term data (Fig. 5) and the results of the MHI observations in 2009–2015. So, in 2009–2011 in the Sevastopol anticyclone region, the oxygen isoline 10 μM was located on the σ_t = 15.60–15.65 kg/m^3 (Fig. 4), and in November, 2015 on the "century" section Cape Chersonese – Bosporus Strait it was much higher – on the σ_t = 15.35–15,40 kg/m^3 (Fig. 5).

The most detailed (the oxygen sensor with the vertical resolution 0.5 m was used) and extensive (the whole northern part of the Black Sea – in Fig. 1 this section is shown by the solid line) investigation of the suboxic zone upper and lower boundaries was got in the 33rd cruise of the R/V "Maria S. Merian" in November, 2013 (Fig. 6, *a*).



a *b*

Fig. 6. Location of the upper and lower boundaries of the suboxic zone (*a*) and the cold intermediate layer (*b*) on the section from the northwestern shelf (on the left) up to the northeastern one (on the right) in November, 2013

The sulfide isoline 3 μM, as well on for the previously considered sections, was located within a very narrow interval between the σ_t = 16.12–16.15 kg/m^3. The oxygen isoline 10 μM is characterized by its higher location in the section western part – at σ_t = 15.75 kg/m^3 than in the section eastern part – at σ_t = 15.85 kg/m^3. Most likely, this is due to more intensive oxygen consumption for oxidation of suspended organic matter. Its high content in the NWS waters is provided by the freshwater runoff, which ensures the phytoplankton growth and subsequent death processes.

The vertical temperature distribution in the σ_t scale was analyzed for the section across the northern Black Sea (Fig. 6, *b*). It exhibits presence of two CIL cores in the western and eastern parts with the minimum temperature 7.83 °C and absence of such a core (i. e. CIL weakening) in the central part at the longitude 34 E.

These features of CIL (the thicker the layer and lower the temperature, the higher the oxygen content in it) did not affect location of the oxygen isoline 10 μM, but became quite well pronounced in position of the oxygen isolines within the 15–50 μM range: these isolines were elevated at the longitude 34° E as compared to the data of the nearest stations. In other words, weakening of CIL and, consequently, decrease in supply of the underlying layers with oxygen resulted in diminution of the oxygen content in them.

The values of the sulfide maximum concentrations in the Black Sea revealed in different expeditions should be considered as an individual problem. Table and Fig. 7 represent the data obtained in 2010–2015. It follows from these data that at the depths exceeding 1700 m, where practically no gradient in the vertical distributions of salinity, temperature and sulfide concentrations is observed [25], the concentration values should constitute about 380 μM. This exceeds significantly the values observed in the 1960–1970s, but does not differ from the values typical of the sulfide concentration at the depth about 2000 m in the 1980–1990s [10]. Thus, the drawn conclusion implies that in course of previous 20 years no significant increase of the sulfide content in the Black Sea near-bottom waters was recorded.

Maximum sulfide concentrations revealed in the MHI expeditions in 2010–2016

Period	Depth, m	Relative density, kg/m^3	Concentration, μM
October, 2010	1743	17.219	378
August, 2011	1250	17.205	354
September, 2013	1750	17.220	379
November, 2013	2136	17.206	382
November, 2015	1801	17.216	384

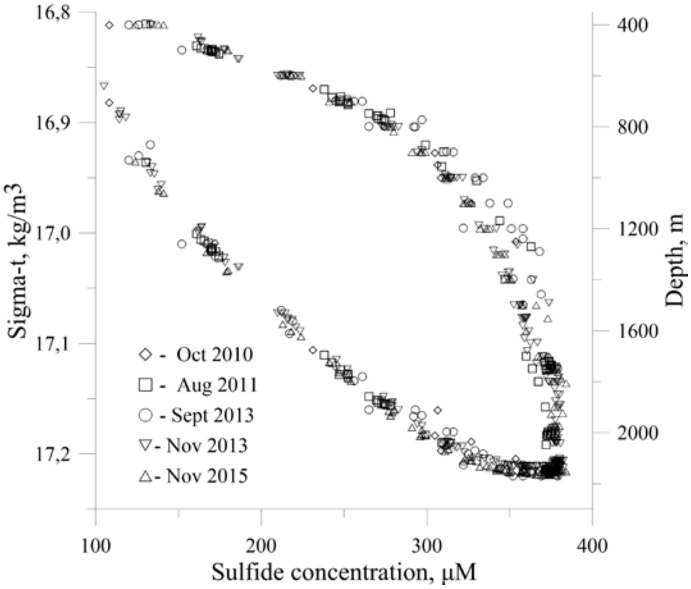


Fig. 7. Vertical distribution of sulfide in 2009–2016 on the depths below 400 m according to the scales of relative density (the lower graph) and depth (the upper graph)

Conclusions

In course of the past 20 years, the sulfide zone upper boundary, defined by the sulfide isoline 3 μM, has not changed its location in the northern part of the Black Sea and is still at the σ_t = 16.10–16.15 kg/m^3. Closer to the NWS, in the Sevastopol anticyclone region the sulfide isoline 3 μM rises to σ_t = 15.9–16.0 kg/m^3; in one case its position was recorded at σ_t = 15.85 kg/m^3.

Location of the suboxic zone upper boundary defined by the oxygen isoline 10 μM is characterized by spatial and temporal variability. In the NWS region where four expeditions were carried out in 2009–2013, the oxygen isoline 10 μM was located within the σ_t = 15.6–15.7 kg/m^3, regardless of the season. In the deep-sea region, in November, 2013 the oxygen isoline 10 μM was located on the

σ_t = 15.7 kg/m^3, whereas in November, 2015 it was much higher – on the σ_t = = 15.35 kg/m^3. Variation of position the oxygen isoline 10 μM observed during 1995–2015 provides no grounds for assessing unambiguously alteration of the suboxic zone thickness in the central part of the sea.

During last 20 years no drastic increase of the sulfide content took place in the Black Sea waters within the depths 1750–2000 m.

It seems reasonable to continue investigations of the suboxic zone and, for this purpose, to carry out a few stations on the continental shelf edge. At that the σ_t = = 16.1–16.2 kg/m^3 should be located in the bottom layer. The sea depth in the points of such stations should be about 150–170 m. Rather flat continental slope to the south off the Cape Tarkhankut or to the south off the Kerch Strait is assumed to be a convenient region for such an experiment.

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