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Current Trends in Oceanography and Marine Science

Kondratev SI Curr Trends Oceanogr Mar Sci: CTOMS-105.

Research Article

DOI: 10.29011/CTOMS-105.100005

Three Typical Hydrological and Hydro Chemical Situations Near the Danube Mouth on the Basis of Field Studies 1997-2013

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Citation: Kondratev SI (2018) Three Typical Hydrological and Hydro Chemical Situations Near the Danube Mouth on the Basis of Field Studies 1997-2013. Curr Trends Oceanogr Mar Sci: CTOMS-105. DOI: 10.29011/CTOMS-105.100005

Received Date: August 22, 2018; **Accepted Date:** 13 September, 2018; **Published Date:** 20 September, 2018

Abstract

Discussed are the spatial distributions of hydrological and hydro chemical (dissolved oxygen, the nutrients) characteristics on north-western shelf (NWS) of the Black Sea near the Danube mouth, obtained in Marine Hydro Physical Institute of RAS research expeditions in 1997-2013. Detailed are three "typical" situations for this area: The Danube flow distribution in the far east or north-east; pressing the drain of the Danube to the west coast of the Black Sea and the alongshore upwelling. In NWS surface waters during photosynthesis takes place rapid and almost complete extraction of silica and nitrate, the latter spent even in early winter. Mineralization processes of particulate organic matter in the bottom waters of NWS are an additional source of silica and nitrates. For silica this process was observed in the warm period, for nitrates even in early winter. Coastal upwelling in the summer can lead to small content of oxygen in coastal waters and cause fish mortality on the NWS.

Keywords: Danger of coastal upwelling; Dissolved oxygen, nutrients; Distributions of hydro chemical characteristics; North-western shelf of the Black Sea, field studies

Introduction

North-Western Shelf (NWS) is one of the Black Sea areas, most difficult to study. This area is influenced not only by the Danube flow, containing the industry wastes of two dozens of European States, but also by contaminated effluent of the Dnieper and Dniester, and so feels extremely strong anthropogenic load [1-6]. Freshwater discharge of four rivers contains plenty of nutrients, this provides of abundant nutrition for phytoplankton in this area throughout the whole year. In the spring-autumn periods in the surface layer of NWS the active consumption of phytoplankton of the main nutrients (inorganic forms of nitrogen, phosphorus and silicon) leads to the formation of oxygen during photosynthesis. In the bottom layer the reverse process occurs - oxygen is actively consumed for oxidation of Particulate Organic Matter (POM) with return of mineral forms of nutrients, as a result of the mineralization. The consumption of large quantities of oxygen on decomposition of POM periodically leads to the hypoxia of bottom waters (oxygen saturation of water less than 30%) in the NWS. Probably the final stage of hypoxia - emergence of hydrogen sulfide after full disappearance of oxygen, with the subsequent fish mortality, caused increased attention to the NWS in the second half of the 20th century. This phenomenon was regularly and repeatedly discussed in the literature [7-16]. All these activities have consistently affirmed the dramatic ecological situation in the NWS with the continuing of fish mortality in summer, but in recent years the encouraging conclusions about improving the ecology of the shelf were appeared [17-18].

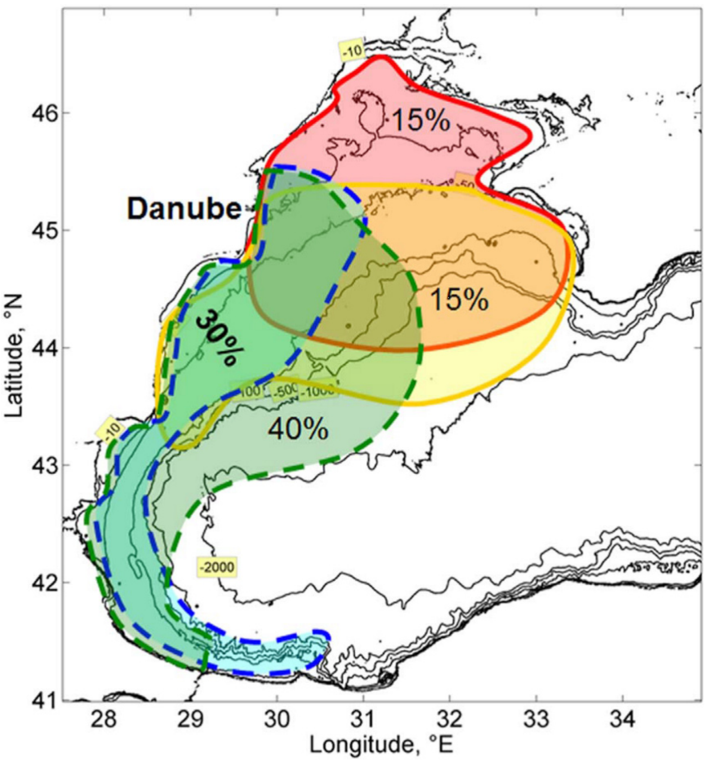
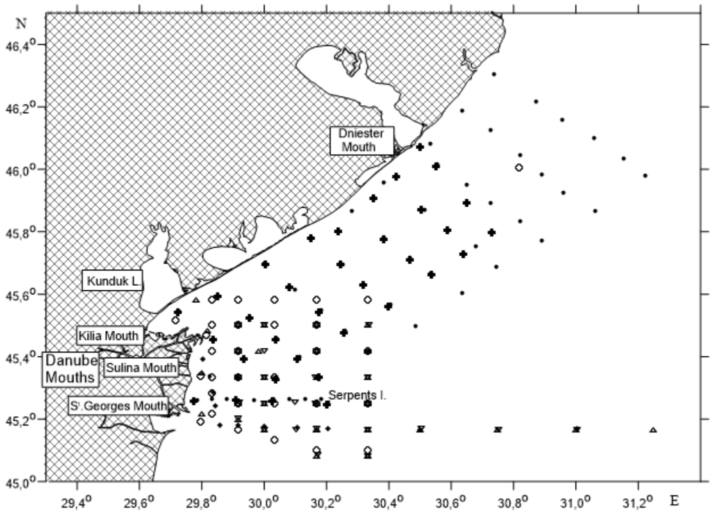


Figure 1: Freshwater runoff infiltration of the Danube in summer according to the distribution of chlorophyll in surface waters.

The most important feature of the north-western shelf of the Black Sea is the presence of estuarine areas of four major rivers (Danube, Dnieper, Dniester, Southern Bug), fresh discharge of them has a significant impact on the patio-temporal variability of the thermohaline structure. A dominant influence on the dynamics and thermohaline structure of waters (variability circulation, intrusion of river waters, upwelling, etc.) have a wind conditions under which water flow quickly adjust to wind flow. A long-term analysis of satellite images of the NWS region made it possible to assess the probability distribution of the freshwater runoff on the shelf. Depending on the wind conditions brackish water can spread east to Cape Tartan, and even to the Cape Chersonese, although more often they follow along the west coast to the Strait Bosporus, (Figure 1).



- September 1997, RV "Trepang" ▽ - October 1997, RV "Trepan"

o - December 1998, RV "Diorit" ◆ - November 2001, RV "Whihr"

✚ - August 2009, RV "Sapphire" ● - October 2010, September 2013 RV "

Figure 2: Map of the research area.

Marine Hydro Physical Institute (MHI) in 1997-2013 researched distribution of hydrological and hydro chemical parameters in this area in 7 expeditions, focusing on the content of dissolved oxygen and nutrients in the surface and near-bottom waters, generalized map of the research area presented in Figure 2. This series of field studies covered three periods: summer, autumn and winter, and occurs at various hydrological situations, the most important in our view are distribution of river discharge in the far north-east; upwelling near Danube mouth along the coast, dramatically changing the content of dissolved oxygen and nutrients in surface waters. Snuggling of the freshwater runoff to the shore not more than 5 miles from the mouth with the proliferation of freshened surface waters to the south along the coast of Romania. This paper describes the features of distribution of hydro chemical characteristics in the wellhead of the Danube area for these three cases.

Materials and Methods

Samples were collected during seven cruises of RV Trepang, Diorite, Whihr in the Ukrainian exclusive economic zones of the northwestern Black Sea, (Figure 2). Investigated parameters were dissolved oxygen, oxygen saturation and nutrients - phosphates (PO_4), silica (SiO_4), nitrates (NO_3), nitrites (NO_2). Surface and bottom water samples were collected with clean plastic bottles making use of a CTD-Seabird, equipped with a Niskin bottles mounted on a rosette frame. After sampling plastic bottles were immediately freeze at -18°C in RV freezer. After cruise (7-10 days) defrosted samples were filtered through 0,45 µm pore size filter Millipore in MHI analytical laboratory, inorganic nutrients (dissolved nitrates, nitrites. silica and phosphates) were determined following standard spectrophotometric methods, [19-20]. Dissolved oxygen was analyzed by standard Winkler titrations on board.

Distribution of river discharge in far North-East

Distribution of streamflow in far east or northeast was fixed in two seasons: early winter at the beginning of December, 1998, and in summer, August, 2009. Run a detailed look at the features of "far" distribution of river streamflow for these two cases. Early in the winter of 1998, the "calm" situation of the winter distribution of hydrological and hydro chemical characteristics was fixed, Figure 3 a-l. Salinity increased smoothly as the distance from the Danube mouths, reaching 17% to 30.2˚ E, about 20 miles from the coast, Figure 3 a. Salinity of bottom waters near the mouths was much larger, 15‰ near the Selina mouth and 11% near St. Georges mouth. However, isohaline 175 in the bottom waters was situated a little further west than at the surface, approximately at 30˚ E. Just as smoothly, as the distance from coast increased temperature, vertical gradient became almost zero after reaching 6˚C at the surface, approximately 10 miles from the coast. Once the salinity reaches 11-12%, relative density of surface and bottom waters became identical, but did not exceed σ_t =13.7 kg/m^3 in all the investigated area. At the same time, the relative water density at shallow (depth of 11 m) station, located to north, opposite the Dniester mouth (30.82˚ N, 46˚ E) reached σ_t =14.0 kg/m^3, i.e. there has already begun penetration of coastal cool water under the less dense water of the open part of the shelf.

Figure 3: Distribution at the surface (a, c, e, g, i k) and bottom (b, d, f, h, j, l) horizons in December 1998: salinity, % (a, b), temperature C˚ (c, d), oxygen saturation, % (e, f), concentrations of: silica (g, h), phosphates (i, j), nitrates (k, l), all in µM.

This "gradual mixing" of fresh and salt water would have to be accompanied by a gradual decrease of all nutrients concentrations from the mouth and practically uniform vertical distribution (except for the stations nearest to the mouths, where salinity of the surface water was noticeably smaller than for the bottom water). Such situation, marked by [21], was really observed for silica and phosphate, (Figure 3). Very high concentrations of both elements in the surface and bottom waters near the Danube mouths where drastically reduced when you remove from the coast. This reduction was accomplished by a relatively uniform distribution near 30.1˚ E. However, the oxidized forms of nitrogen were not respected to "conservative" distribution, i.e. a smooth decrease with an increase in salinity. Nitrate in surface and bottom waters decreased sharply by isohaline about 13%, and further to east remained at the level of 2 μM across all water thickness. Nitrite concentration, on the contrary, all over all area were within range 0.4-0.5 μM, and only in surface waters near Selina mouth increased to 0.8-0.9 μM.

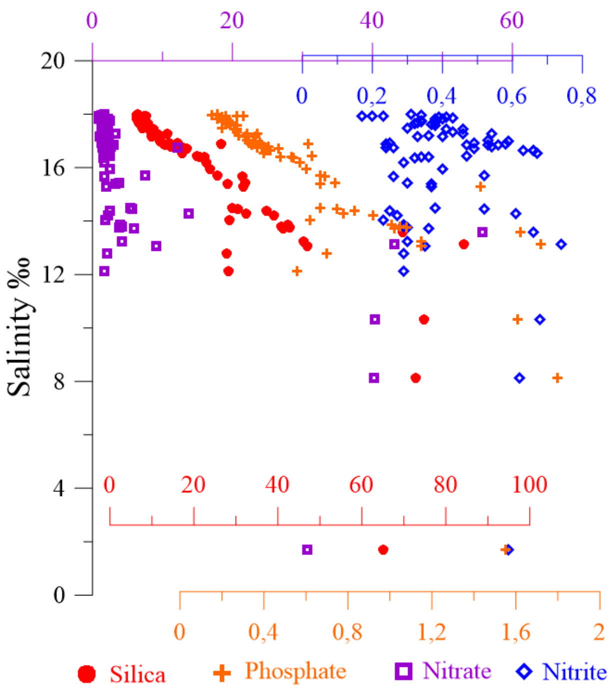


Figure 4: The distributions of silica, phosphate, nitrate, and nitrite, all in μM.

Marked differences in behavior of nutrients when mixing in the winter of 1998 were confirmed by changes of concentrations of four forms of biogenic elements with increasing salinity, Figure 4. For silica and phosphate there was practically a linear relationship between concentrations and salinity after salinity increased more 12%. About oxidized forms of nitrogen the situation is somewhat different: the content of nitrates in waters reduced almost in 10 times after salinity becomes more 12%, whereas nitrite concentrations were almost independent of salinity. Considerable variation in the concentrations of nitrate, phosphate and silica in brackish (4-10%) waters can be attributed to sampling in various parts of the investigated area. If in stations were located as a compact group across from each of the three mouths west of 30˚ E, in December 1998 polygon dimensions were considerably more. Removing of nitrate from river runoff with simultaneous conservative behavior of silica suggests that in early winter the processes of photosynthesis has not stopped completely, but silicon containing phytoplankton (diatoms) was not involved in them. Thus, the diatoms growth requires not only the minimum content of silica on the level 2 μM but also a certain temperature, whereas other types of phytoplankton are not so demanding of conditions. This assumption of the continued processes of photosynthesis is also confirmed by data for the oxygen saturation of water. In the open part of the shelf saturation of surface water was 97-98%, whereas near the coast it was higher, reaching 100-102% opposite the Selina branch and 108-110% opposite Kilia branch, (Figure 4). e, f. If water saturation 100-102% can be attributed to a decrease in oxygen solubility with increasing salinity of river flow mixing with sea water, high 108-110% saturation indicates that, despite the low water temperature 2-3˚C, photosynthesis in bay near Kilian branch, protected from westerly winds, haven't stopped completely. Mineralization processes in bottom waters for POM also continued: almost at the same temperature and salinity, oxygen saturation in surface waters to the East of 30˚ E was not less than 97%, whereas in bottom waters it is not exceed 94-95%. Continued processes of photosynthesis in winter in the NWS is confirmed by satellite data on the distribution of chlorophyll "a" in surface waters at this time of year [22]. In this work it was concluded that the intensity of the bloom of phytoplankton in the cool winters is at 50% higher than in the warm August 2009. Situation of the maximum influence of freshwater runoff on the distribution of hydrological and hydro chemical characteristics in the summer was been observed in the August 2009. If in the winter 1998 Danube discharge strongly influenced on vertical gradients of temperature and salinity only on the nearest area to the mouth (west of 30°E), in summer 2009 surface and bottom water differed significantly on temperature and salinity all over the polygon, a-d. Salinity of freshened surface [23]. waters did not exceed 15%, and was not less than 17.5% at the bottom. The surface water temperature was around 24-25˚C, while the bottom only about 10-12˚C. Feature of the hydrological structure was freshened warm lens (bottom water temperature in the lens was more than 20˚C) about 15 miles in diameter and thickness of about 20 meters, which was located at 30.5˚ E, 45.5˚ N. Content of certain hydro chemical component in bottom waters of this lens was significantly different from the others.

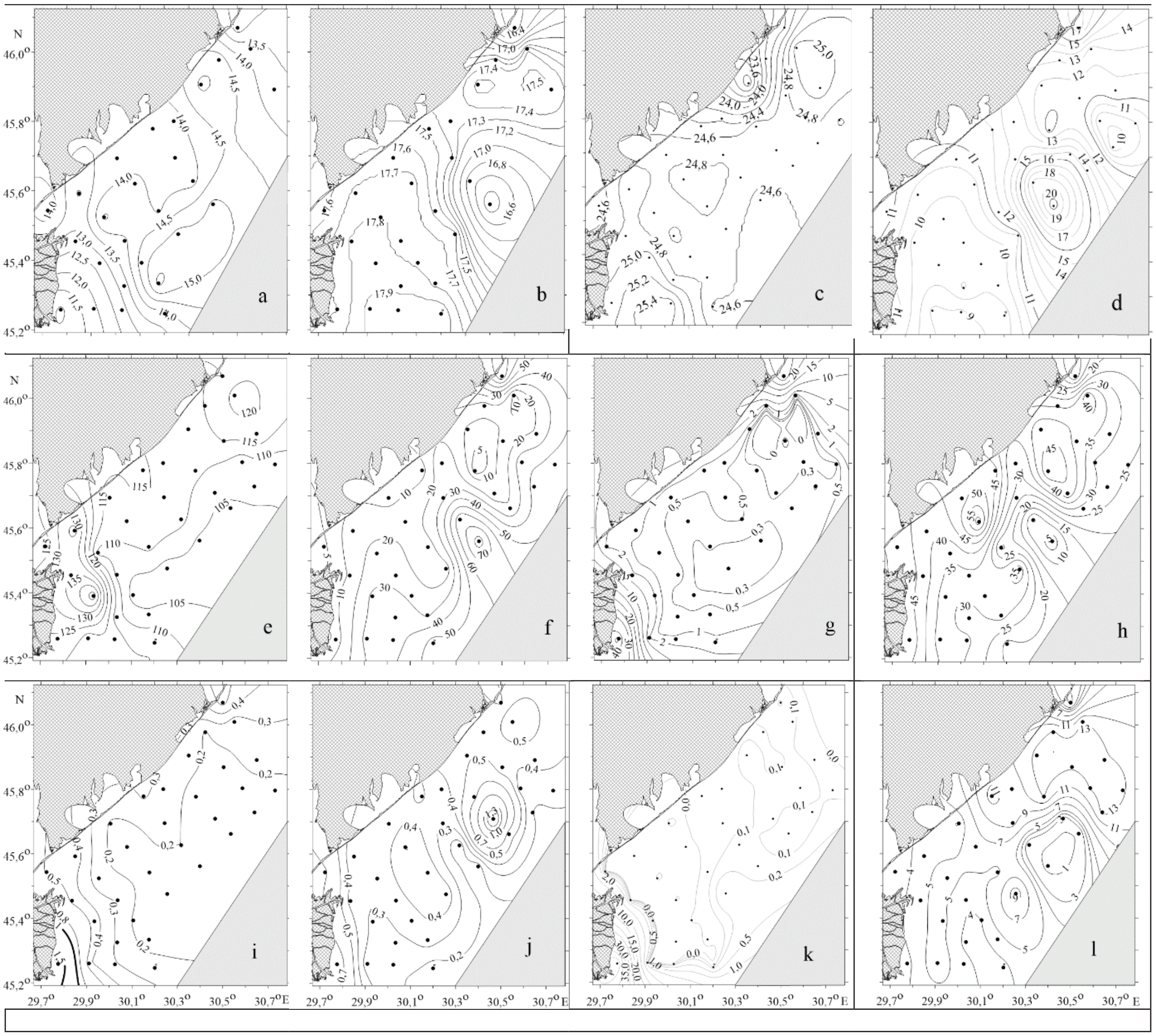


Figure 5: Distribution at the surface (a, c, e, g, i, k) and bottom (b, d, f, h, j, l) horizons in August 2009: salinity, % (a, b), temperature C° (c, d), oxygen saturation, % (e, f), concentrations of: silica (g, h), phosphates (i, j), nitrates (k, l), all in µM.

Photosynthesis in surface waters provided water oxygen saturation at least 105% throughout the all area, in some area near Kilia mouth saturation exceeded 135%, Where as in the bottom waters consumption of oxygen on POM mineralization led to extensive hypoxia on all over the polygon (except lens of freshened water) with saturation less than 30%, and in coastal areas, saturation dropped to 5%, (Figure 5). Bottom waters sampling occurred at a depth of 1 m, so it is possible that near the bottom hydrogen sulfide could appear. Active photosynthesis in warm surface waters quickly “ate” silica and nitrate, reducing their content in 10 miles from the mouth approximately 100 times compared the flow of the Danube. A similar decrease was observed for concentrations of phosphate, but reducing of concentrations was lower, approximately 10 times. The return of inorganic form of silicon in mineralization processes ensure the content of this element in the bottom waters of 30-40 µM, which is comparable with the silica concentrations in runoff. Content in bottom waters of nitrate 5-10 µM has not reached the level of 35 µM in the Danube discharge, but was approximately 50-100 times higher than those in surface waters. Significant differences for the phosphate content in the surface and bottom waters were not observed. Distribution of nitrite in surface and bottom waters was very similar to the distribution of nitrate, but in lower concentrations. When removing from the mouths to the east the concentration of nitrite (max. 1.7 µM near S^t. Georges branch) rapidly decreased, becoming zero at about 1 µM isocline for nitrates. Nitrite concentration in the bottom waters were higher than on the surface, about 0.2-0.5 µM. In the freshened lens with the center at 30.5° E, 45.5° N content of oxygen and nutrients on the surface did not differ from the surrounding waters, but the bottom water contained more oxygen (70% saturation in lens vs. 30%

around), less silica (5 µM vs. 30-50 µM), less nitrate (about 1 µM vs. 5-7 µM), but more phosphate (more than 1 µM vs. 0.3-0.4 µM). It can be expected that in the bottom lens water mineralization processes started, but have not reached such intensity, as in most parts of the polygon.

Upwelling along the coast near Danube mouths

In seven MHI expeditions on 1997-2013, in three cases the upwelling in the coastal strip was observed, the most contrasting change in the distribution of hydrological and hydro chemical characteristics occurred in September, 2013. Brackish surface waters with salinity 16.5-16.6% and temperature 18-19˚C near the shore were replaced by the bottom waters of the open part of the shelf with a salinity of about 18‰ and temperature 9-10˚C, Figure 6 a-d. During the removing of surface waters from the coast, two lenses of freshened and warm waters (salinity near the bottom less than 17.5% and temperature over 15˚C) were formed, b, d, one opposite the Dniester mouth, another centered on 45.7˚ N, 30.6˚ E, both with a diameter of about 20 miles and a thickness of about 20 m. Content of oxygen and silica in near-bottom waters of these lenses is markedly different from the background. It should be noted, that in September, 2013 in this shelf area, rich by nutrients, oxygen super saturation of surface water was expected. Indeed, the surface waters oxygen saturation in south-east of the investigated area, not affected by upwelling, was about 105%, (Figure 6). However, the wake up of bottom waters, depleted by oxygen 50%, f, to the surface led to ecologically alarming situation when the oxygen saturation does not exceed 80% in the entire water column 2-3-miles of coast south-west of the Dniester mouth, Figure 6 e. It can be assumed that such upwelling's, waked up to the surface even less oxygen-rich bottom water, caused fish mortality regularly encountered in the area earlier.

Figure 6: Distribution at the surface (a, c, e, g, i, k) and bottom (b, d, f, h, j, l) horizons in September 2013: salinity, % (a, b), temperature ˚C (c, d), oxygen saturation, % (e, f), concentrations of: silica (g, h), phosphates (i, j), nitrates (k, l), all in µM.

The greatest influence on the content of nutrients in the surface waters, upwelling provided for silica, whose contents in surface waters was at the level of 1 μM (remained in south-east), and has increased by more than an order of magnitude near the shore Figure 8 g. This confirms the conclusions of the additional source of silica for surface waters near the Danube mouths. Notable changes in the concentration of phosphate as a result of upwelling were not observed mainly due to low concentrations of less than 0.1 μM in the surface and bottom waters. Not too changed also the concentration of nitrate, however, it should be noted, that the concentration of nitrates in the bottom waters 4-5 μM were higher than on the surface 2-3 μM, so, the processes of mineralization in the bottom waters serve as a source for surface waters not only of silica but also of nitrate.

Snuggling of the freshwater runoff to the shore

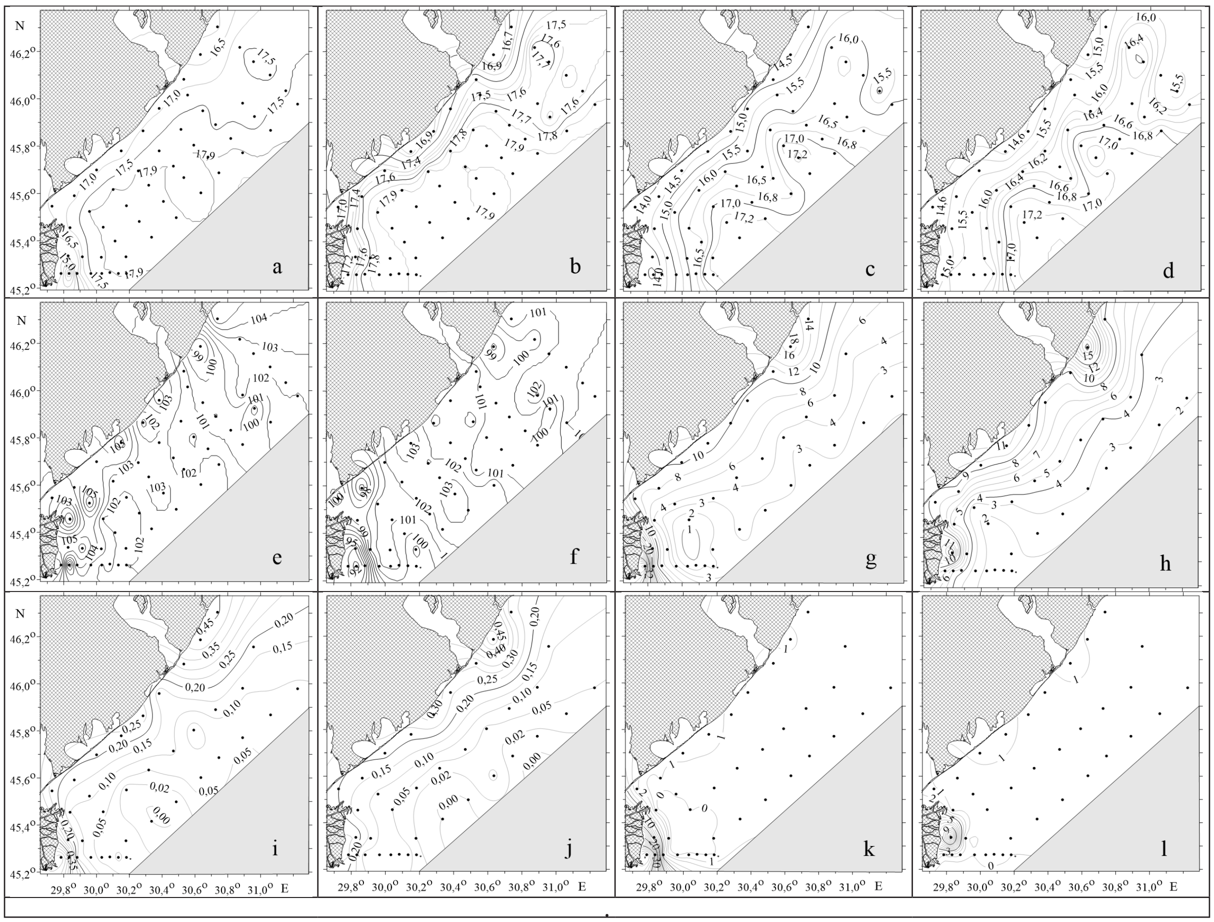


Figure. 7. Distribution at the surface (a, c, e, g, i, k) and bottom (b, d, f, h, j, l) horizons in October 2010: salinity, % (a, b), temperature C° (c, d), oxygen saturation, % (e, f), concentrations of: silica (g, h), phosphates (i, j), nitrates (k, l), all in μM.

The situation with the localization of Danube flow in a narrow alongshore strip due to the action of winds was observed in October 2010, when nearly all the area was filled with the waters of the open shelf, and freshwater runoff was pinned to the shore, Figure 7 a-l. Salinity of surface water less than 17.5%was only in the alongshore band in 10-15 miles from the Danube mouths, the rest of the polygon has salinity generally higher than 17.9%, Figure 7 a. This determined the distribution of nutrients: silica and phosphate near the shore were more than 8 and 0.2μM, respectively, while in the waters of the open shelf (and on the surface, and near the bottom) concentrations were less almost an order of magnitude, (Figure 7). g-j Vertical distributions of all hydrological and hydro chemical characteristics were practically monotonic, differences between surface and bottom waters from were observed only in the 3-mile zone adjacent to the Selina and S^{t}. Georges mouths. Among the features of the individual hydro chemical characteristics content it should be noted: "safe" oxygen saturation of surface and bottom waters at 100-102%;very small concentrations of all nutrients in the waters of the open part of the shelf: silica on the level of 2-3 μM; nitrate less than 1 μM; phosphate on the level 0.1 μM, whereas at the nearest to S^{t}. Georges station surface waters contain: silica 49 μM; nitrates 49 μM; phosphate 0.69 μM. Temperature of the shelf waters 16-17°C and solar irradiance in early October were quite sufficient to ensure flash bloom of phytoplankton, but low concentrations of nutrients were not allowed to saturate the surface waters by oxygen more than 102-103%. So in this particular moment of October 2010 the NWS water did not differ from the water of the deep sea (except for the 3-mile zone near S^t. Georges mouth), in other words, we have fixed the time of "ventilation" of NWS waters in autumn. In all the above cases (extension and locking of the freshwater runoff, upwelling) differences in the degree of water oxygen saturation had the biggest impact on the content of silica; in some cases, with hypoxia in the bottom waters concentrations of silica exceed its content in surface waters. This coincides with the conclusions of about additional source of inorganic silicon in warm season through mineralization of organic forms of silicon, brought by the flow of the Danube and deposited during the transformation of the river waters.

Conclusion

Waters of the open part of the Black Sea, filled the NWS in autumn and snuggled freshwater runoff to the shore, contained low concentrations of nutrients, particularly low concentration of silica should be allocated. This indicates the continuation of a dangerous process of change in phytoplankton species composition and throughout the full food chain in the Black Sea. In NWS surface waters during photosynthesis takes place rapid and almost complete extraction of silica and nitrate, the latter spent even in early winter. Coastal upwelling in the summer can lead to small content of oxygen in coastal waters and cause fish mortality on the NWS. Mineralization processes of POM in the bottom waters of NWS are an additional source of silica and nitrates. For silica this process was observed in the warm period, for nitrates even in early winter. Silica content in bottom waters was even higher than at the station nearest to the S^t. Georges mouth. Distributions of phosphate and nitrite in surface and bottom waters on the NWS are not too dissimilar. For phosphate this is connected probably with rapid turnover in the processes of photosynthesis and oxidation of POM. For nitrite - perhaps because it is an intermediate product of nitrification and denitrification processes.

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