Peculiarities of Nutrients Distribution in the Coastal Waters near the Danube Estuary in 1997–2013

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Results of analysis of spatial distribution of the nutrient cycle elements in the coastal waters of the Danube region carried out based on the expeditionary research performed by the Marine Hydrophysical Institute in 1997–2013 are represented. Constant inflow of inorganic forms of the nutrient cycle elements (nitrogen, silicon and phosphorus compounds) to the Black Sea northwestern shelf due to the Danube, Dniestr and Dnieper waters provides rich forage reserve for phytoplankton in course of a year. In spring-autumn period in the surface layer of the Danube estuary region the photosynthesis process is accompanied by oxygen generation; and in the bottom layer oxygen is actively spent for oxidation of the precipitated suspended organic matter that periodically results in the bottom hypoxia. Thus in the surface layer phytoplankton consumes the main biogenic cycle elements, whereas in the bottom layer these elements are released due to the organic matter destruction. Influence of different hydrological situations occurring in the estuary region upon spatial distribution of the hydrochemical components is considered. The most important three cases are noted: 1) if the Danube waters propagate rather far (30–50 miles) to the east content of nutrient elements in the oxygen over-saturated surface waters is much lower than in the oxygen under-saturated bottom layers; 2) if the Danube waters are "closed" within the narrow along-coastal belt and the whole estuary region is filled with the open shelf water, practically uniform vertical distribution of nutrient elements is observed beyond the 2–3 mile along-coastal belt; 3) in case of upwelling, the elevated to the surface oxygen under-saturated waters propagating at 20–30 miles off the coast contain much more nutrient elements than the surrounding waters.

Keywords: coastal waters near the Danube estuary, hydrological features, oxygen saturation, hypoxia, nutrients of the main biogenic cycle, expeditionary data of 1997–2013.

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Introduction. Coastal waters near the Danube estuary are one of the most complicated regions of the Black Sea for research. The region is affected not only by the Danube input containing the waste products of industry and life activities of ten countries in Europe, but also the polluted inflow of the Dnieper and Dniester, and therefore contains extremely strong anthropogenic impact [1 – 6]. With the freshwater runoff enters a large amount of biogenic nutrients that provides an abundant food base for the phytoplankton in this region during the year.

The dynamics of the coastal waters near the Danube mouth is determined primarily by wind, surface currents change direction very quickly, adapting to changes in the wind field [7]. This region is also complicated from the viewpoint of hydrochemistry. It is relatively common only in the winter when the Black Sea Rim Current captures the entire north-west shelf and "ventilates" it, carrying the Danube runoff to the south. During all other seasons the biogenic nutrients, coming in significant quantities with the Danube runoff, remain in the coastal waters [8, 9].

There is an active formation of oxygen in the surface layer of the Danube coastal waters during photosynthesis in spring-autumn period, but in the bottom layer oxygen is actively consumed due to the oxidation of the sinking particulate organic matter, which occasionally leads to the bottom hypoxia, regularly observed in the area and have repeatedly been discussed in the references [10 – 13].

Thus, active consumption of the nutrients of the main biogenic cycle (nitrogen, silicon and phosphorus compounds) by phytoplankton takes place in the surface water layer, and in the bottom - release of these elements as a result of the organic matter destruction.

In the previous article the influence of hydrological structure features on the spatial distribution of oxygen in the coastal waters near the Danube mouth was discussed, and it was concluded that bottom hypoxia occurs, as a rule, when in the shelf waters thermocline and halocline exist in combination [14].

The present research, based on the data of Marine Hydrophysical Institute (MHI) cruises of 1997 – 2013, covers the influence of oxygen distribution in coastal waters near the Danube mouth on nutrients distribution, i.e. phosphate, silicate and inorganic forms of nitrogen (ammonium, nitrite and nitrate).

Data and methods. Research of the coastal waters near the Danube mouth were carried out by Marine Hydrophysical Institute in September and October, 1997 on R/V *Trepang*, December 1998 on R/V *Diorit*, November, 2001 on R/V *Vihr*, August 2009 on R/V *Sapfir*, October 2010 and September 2013 on R/V *Professor Vodyanitskii*. Hydrochemical observations were performed under the station network, displayed in Fig.1 See the more detailed scheme of stations for each particular cruise on the figures demonstrating distribution of the nutrients.

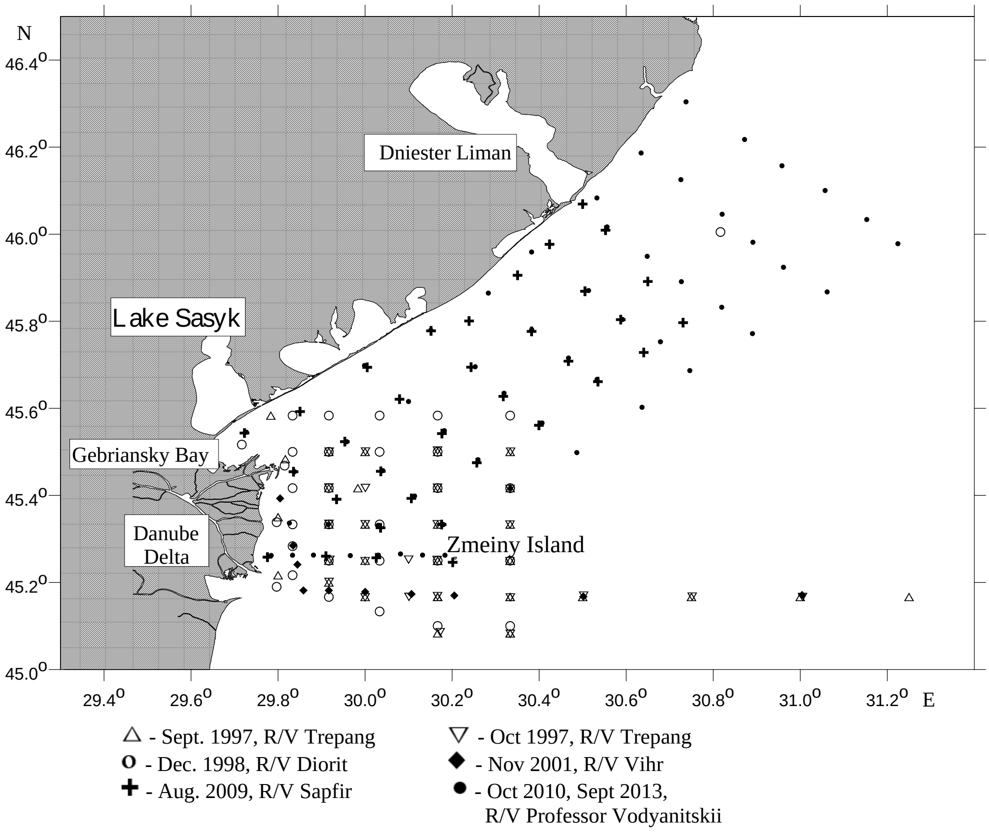


Fig. 1. Station network covered by Marine Hydrophysical Institute in coastal waters in the Danube plume area in 1997 – 2013

The TS measurements were made by the CTD system. Water sampling at bottom (0.5 – 1 m from bottom) and surface (0 – 1 m) levels were carried out by the cassette of plastic bathometers. Water samples in 250 ml plastic containers were immediately frozen until analyzed for nutrients (nitrate, nitrite, phosphate and silicate) concentrations. The analytical laboratory of the MHI Sea Biogeochemistry Department performed the chemical analyses reported here. Storage time was usually less than 14 days.

The chemical data were processed by standard methods recommended for the ocean hydrochemical research [15]. To calibrate the instruments certified reference materials, produced by Institute of Physical Chemistry, National Academy of Sciences of Ukraine, were applied.

Results and discussion. In the present paper nutrients distribution in the surface and bottom coastal waters near the Danube mouth will be considered against the background of the dissolved oxygen distribution, obtained in the same expedition and at the same stations listed in the part *Data and Methods*.

September 1997. Size of the article does not permit to show the oxygen and nutrients distributions in the surface and bottom coastal waters near the Danube mouth in September and October 1997, presented in [11, 16, 17]. The most interesting results will only be mentioned.

Thus, in September 1997 the significant oxygen supersaturation was observed in surface coastal waters of the Danube estuary region 20 × 30 miles (saturation more then 120 % compared with 105 % background at the periphery of the investigated area). This area was marked by an increased content of phosphate (0.1 – 0.2 μm under the background 0.3 – 0.4 μm), silicate (0.5 – 1.0 μm under the background 2 – 3 μm) and nitrate (less 0.1 μm under the background 0.2 μm), while the nitrite concentration was 0.1 – 0.2 μm and didn’t differ from the background values.

In September 1997 under the surface area of oxygen supersaturation was located the hypoxia zone with oxygen saturation less 30 % (under the background 70 %). This part was marked by considerably higher concentrations of phosphate (0.25 – 0.40 μm under the background 0.1 – 0.2 μm), silicate (24 – 28 μm under the background 12 – 15 μm), nitrate (10 – 12 μm under the background 1 – 2 μm), whereas the higher concentration of nitrite was not found (its content was in the range of 0.2 – 0.5 μm within the whole researched area).

The observed qualitative correlation between the water oxygen saturation and nutrient content was recorded repeatedly [10, 12 – 14] and was relatively simple to explain. Oxygen supersaturation of surface waters is the result of intensive photosynthesis, when the nutrients are consumed by phytoplankton. Under a deficite of oxygen in the near-bottom waters the mineralization of the sinked organic matter is activated, resulting in the nutrients return to dissolved form. The difference in the nutrients concentrations in the surface and near-bottom layers is the most contrasting for the situations with weak water dynamics, when the phytoplankton in surface waters "have time" to consume nutrients before entering the new ones with the Danube runoff, and the near-bottom waters have no inflow from the open shelf.

October 1997. In September 1997 the strong vertical stratification of salinity and temperature in the coastal waters near the Danube mouth led to the nutrients distribution where low concentrations at surface and high concentrations at bottom were observed. In October the continuous northwest wind led to the shift of surface water to the east and caused a powerful alongshore upwelling (see. in paper [16] for details). Thus, the Danube water runoff, being not completely transformed, extended to the all research area and provided salinity of surface water less than 17 ‰, while the bottom layer was occupied by the Black Sea water runoff with salinity over 18 ‰. This provided another typical distribution of hydrochemical elements.

In surface water the influence of freshwater runoff become weaker from the Danube estuary to the east and the concentrations of oxygen and nutrients decreased gradually: oxygen saturation from 140 % to background 106%, silicate concentration from 7 to 1 μm, phosphate from 0.6 – 0.7 to 0.1 μm, nitrate from 5 – 7 to 1 μm and less, nitrite from 0.6 – 0.7 to 0.1 μm. These changes took place within 29.9° E and 30.2° E (in October the research area was situated to the east of 29.9 °E). High concentrations of nutrients in the surface layer of supersaturated oxygen waters of the coastal region can be accounted for incomplete extraction of nutrients delivered in excess by the Danube runoff.

At the near-bottom level due to the water inflow from the open shelf, the oxygen saturation increased to at least 50 %, which provided relatively uniform distribution of nutrients. On the greater part of the investigated area silicate concentration was within the range of 15 – 18 μm (earlier in Sept in hypoxia zone the concentration was above 25 μm), phosphate – within the range of 0.10 – 0.15 μm (earlier 0.25 – 0.40 μm), nitrate – within the range 3.5 – 45 μm (earlier 10 – 12 μm), nitrite – within the range 0.1 – 0.2 μm (its content remain substantially the same as in September 1997).

All the aforementioned peculiarities of the distributions appeared also in a latitudinal section across 45°N10', where the influence of the Danube runoff, providing a higher degree of oxygen saturation and high nutrients concentrations, were observed only in the western part of the section. While to the east of 30.2 °E almost homogeneous vertical profiles of all components were found with a gradual decrease of oxygen saturation and increase of nutrients content with the depth.

December 1998. In December the Danube runoff become apparent almost in the whole researched area. Thus, 16 ‰ isohaline, considered to be the contour of transformed river water in the northwestern part of the Black Sea [18], in surface waters located along 30.15 °E, in the near-bottom ones – along 28.85 °E. The salinity of the surface waters gradually increased from the estuary to the east from 3 – 4 to 17 ‰, and temperature of the waters increased from 2 °C near coast line to 9 °C in the east (30.3 °E).

This Danube runoff propagation has determined the distribution of oxygen and the nutrients. The content of oxygen and nutrients in surface waters significantly decreased from the Danube estuary to the east till 30.2 °E, and in the near-bottom waters – till 29.9 – 30.0 °E, eastward of these borders relatively homogeneous distribution of all the components was observed. Decrease of the oxygen concentration in this case was mainly due to the physical process of the water temperature increase moving from coast line, because the degree of oxygen saturation remained the same almost the entire water area: 97 – 100 % in surface waters and 94 – 96 % in the near-bottom ones. Almost the homogeneous vertical oxygen saturation throughout the entire water column signified slight differences in the redox conditions at the surface and near-bottom levels under relatively low temperature which slowing down the photosynthesis.

The oxygen saturation of surface waters over 100 % was revealed only in the narrow alongshore stripe, where increase of salinity reduced the solubility of gases (Fig. 2, *a*). In this area the highest concentrations of nutrients were found quite expectedly. Thus, on the station closest to the Danube mouth, the freshened surface waters had the following concentrations: phosphate – over 3.5 μm (in the east of the research area – 0.2 – 0.3 μm); silicate – over 90 μm (in the east – 8 – 10 μm); nitrate – over 120 μm (in the east – 2 – 3 μm) (Fig. 2, *b* – *d*).

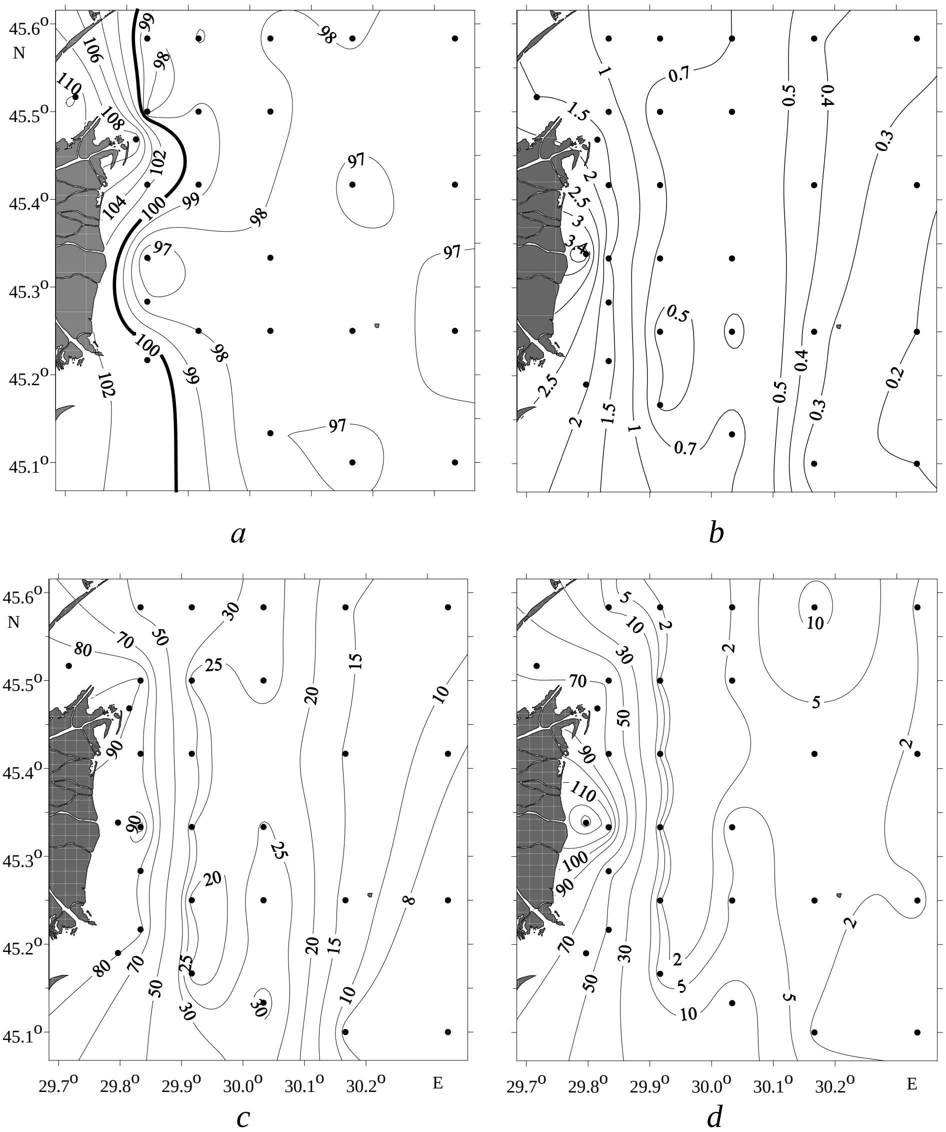


Fig. 2. Surface distributions of the (*a*) oxygen saturation (%), (*b*) phosphate, (*c*) silicate, (*d*) nitrate, all (μm) in December 1998

In the near-bottom waters the slow processes of organic matter mineralization resulted in the same degree of oxygen saturation 94 – 96 % almost all over the research area; higher saturation was observed in the incompletely transformed coastal waters with salinity less than 16 ‰ (Fig. 3, *a*). Under almost the same oxygen saturation of near-bottom waters, the nutrients content didn't vary with such contrast, as in surface waters: phosphate – 0.8 – 0.9 µm near the estuary and 0.2 – 0.3 µm in the east of the research area; silicon – 35 – 40 µm near the estuary and 7 – 8 µm in the east; nitrate – 4.5 – 5.0 µm near the estuary and about 2 µm in the east (Fig. 3, *b* – *d*).

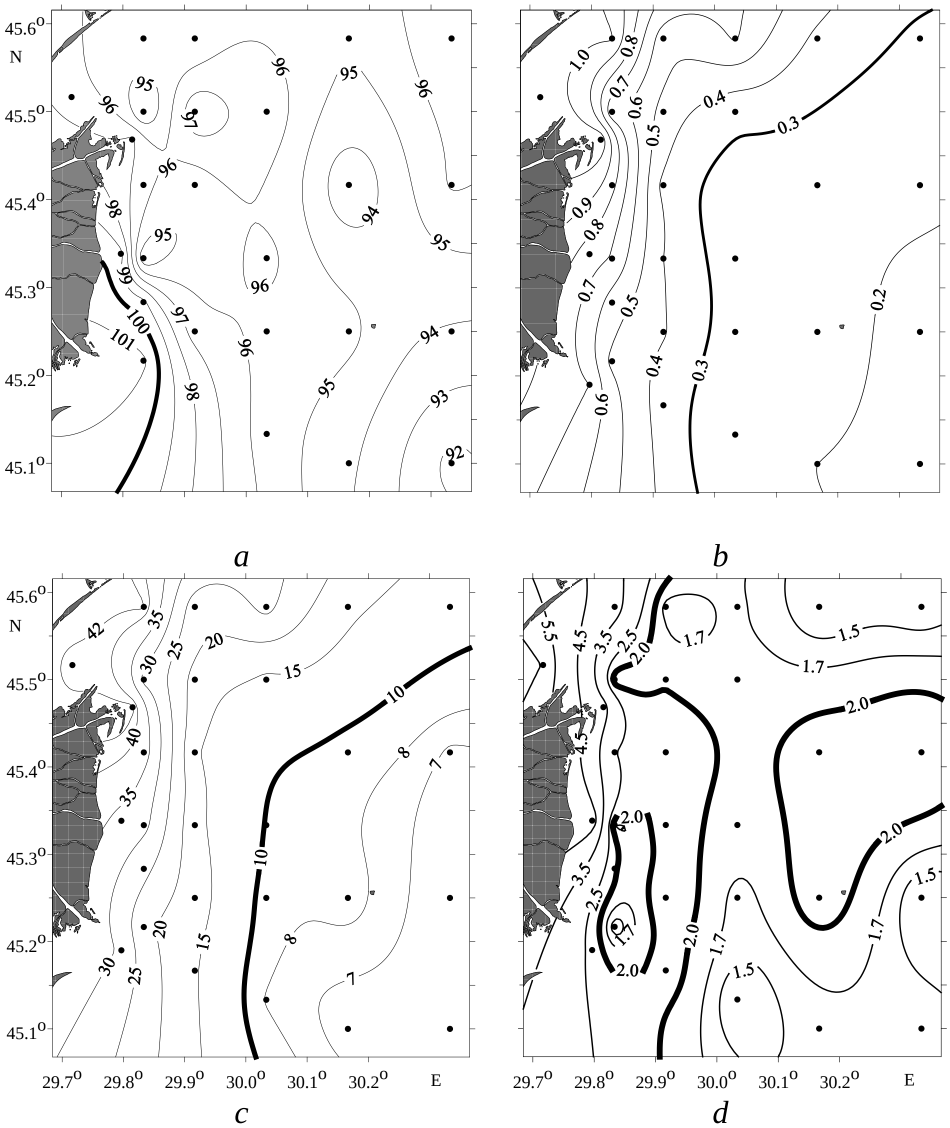


Fig. 3. Near-bottom distributions of the (*a*) oxygen saturation (%), (*b*) phosphate, (*c*) silicate, (*d*) nitrate, all (µm) in December 1998

Water salinity increase as the moving off the coast hasn't great influence on the nitrite distribution. In surface waters near the estuary the concentration of nitrite was 0.7 – 0.8 µm and exceeded twice the background concentration of 0.4 µm. There was no difference in the nitrite concentrations in near-bottom waters in the east and west of the research area, everywhere were the values 0.3 – 0.4 µm and only at 29.9 °E small area of concentrations 0.5 – 0.6 µm was found.

Figures 2 and 3 reflect apparently "ideal" picture of the Danube runoff impact on the distribution of hydrological and hydrochemical features in the estuarial area in winter. During this period of weakened water dynamics [9] and also, due to the low water temperature, slowing of the biochemical processes in surface (photosynthesis) and bottom (decomposition of deposited organic matter) waters are typical. It results in almost the same degree of oxygen saturation everywhere (see above). Consequently, the nutrients delivered with the Danube runoff were probably almost unconsumed during photosynthesis.

November 2001. The survey of the section 45 °N 10' in November 2001 was performed after upwelling appeared as a result of the prolonged north-eastern wind. Hence, the cool freshened waters having temperature less 11.3 °C and salinity less 17 ‰ filled the western part of the section and propagated in 20 metre water column somewhere at 30.3 °E [19].

There was observed relatively homogeneous vertical distribution of oxygen (about 6.5 ml/l) and degree of the oxygen saturation (about 93 – 95 %) at the section at 45 °N 10' in the upper 15 – 20 metre water column. It should be noted that for the first time within the whole research area (even near the estuary) degree of the oxygen saturation was lower than 100 %. The most important peculiarity of the vertical oxygen distribution at the section 45 °N 10' was a small area of hypoxia (which was possible to appear earlier in summer) at 29.9 °E on the 26 – 28 metre depth having oxygen saturation less than 40 % (see article [19] for details).

In this area of hypoxia the content of phosphate, silicate and nitrate significantly exceeded the background values (phosphate – over 0.5 µm when the background – 0.2 – 0.3 µm; silicate – over 10 µm when the background 2 – 3 µm; nitrate – over 4 µm when the background 1 – 2 µm). At the same time the nitrite concentration 0.02 – 0.03 µm in the area of hypoxia was even less than the background one – 0.06 – 0.10 µm.

Appearance in the given region of the hypoxia area with high concentration of phosphate, silicate and nitrate could be explained not only by the processes of mineralization of organic matter, but also by the penetration of oxygen-depleted deep-sea waters [5, 6, 20]. But in this case higher concentrations of the components listed above should be observed in the near-bottom waters throughout all the section that, however, is disproved by the above mentioned features of their distributions. Consequently, hypoxic area discovered in late autumn is the result of a purely biochemical processes in the Danube estuary region.

August 2009. Oxygen and nutrients distributions in the surface and near-bottom waters near the Danube estuary in August 2009 were very similar to the results of the survey in September 1997.

The intense photosynthesis have provided more then 110 % oxygen saturation in the surface water almost everywhere (the background 105 % in east) (Fig. 4, *a*) and was accompanied by "grazing" of nutrients, and as for the oxidized forms of nitrogen this "grazing" was almost complete (Fig. 4, *b* – *d*).

But the near-bottom waters for the greater part of the research area were in a state of hypoxia with oxygen saturation below 30 % (Fig. 5, *a*), nutrient concentrations were significantly (several times) higher than those on the surface (Fig. 5, *b* – *d*). Moreover, the silicate concentrations in the near-bottom waters were even higher than in the surface on the station closest to the Danube mouth!

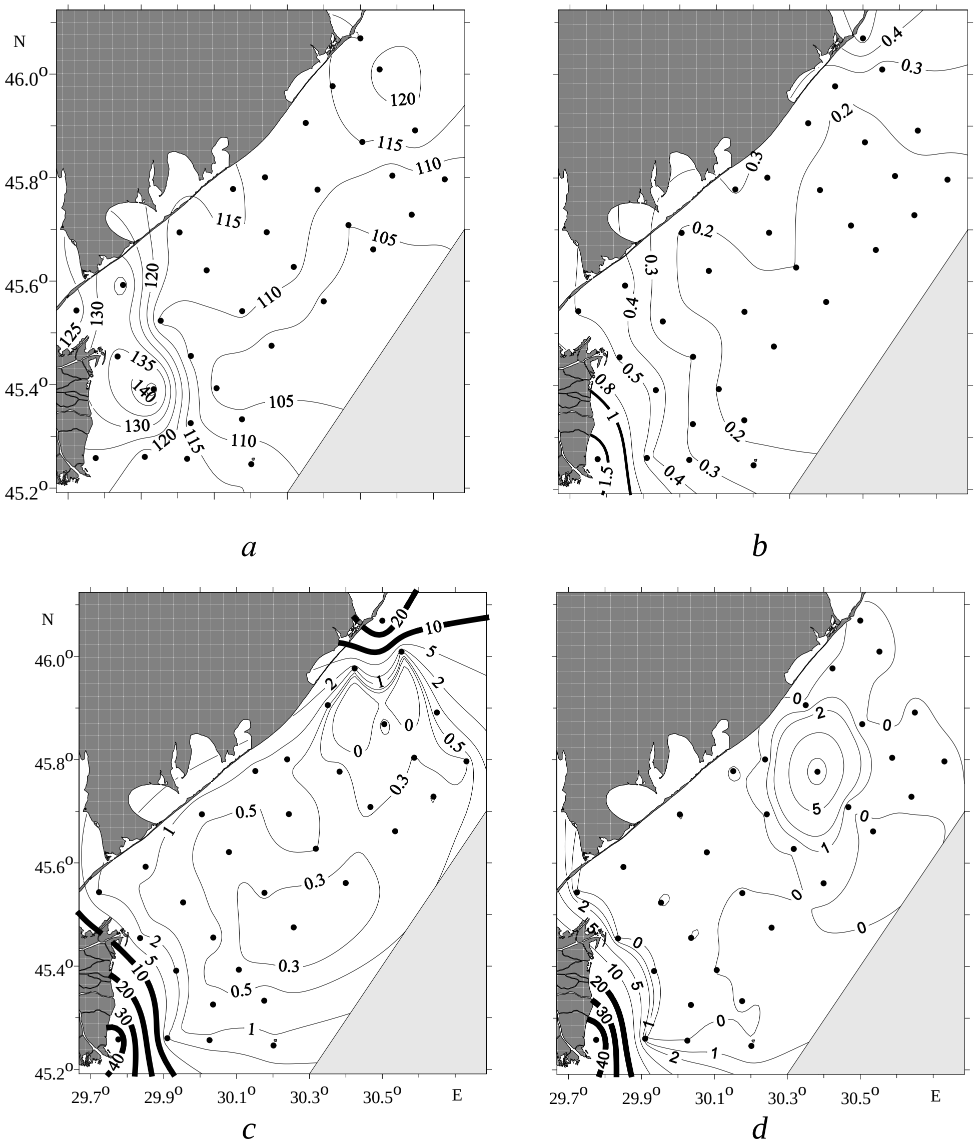


Fig. 4. Surface distributions of the (*a*) oxygen saturation (%), (*b*) phosphate, (*c*) silicate, (*d*) nitrate, all (μm) in August 2009

It should also be noted that at the relatively shallow station in the northeast disappearance of hypoxic conditions and increase of oxygen saturation in the near-bottom waters up to 70 % were accompanied by a significant decrease in the amount of nutrients compared to the waters nearby.

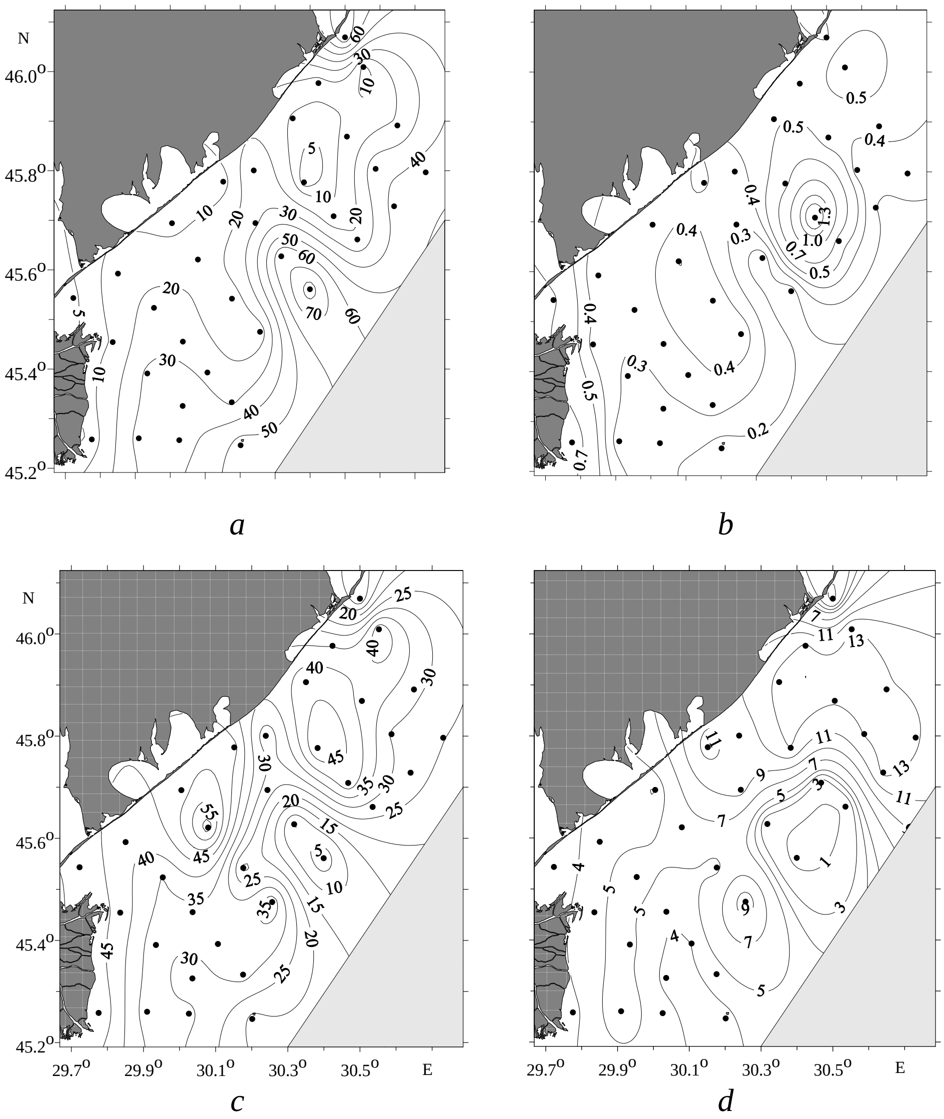


Fig. 5. Near-bottom distributions of the (*a*) oxygen saturation (%), (*b*) phosphate, (*c*) silicate, (*d*) nitrate, all (μm) in August 2009

October 2010. In October 2010, almost the whole investigated area throughout the all water column was filled with the open shelf waters with relatively high salinity (over 17 ‰), the effect of the river runoff was felt only in the upper 5 m of the alongshore areas [21]. This situation was a result of the combined action of currents, one of which as a narrow stream going alongshore to the southwest, and did not allow freshwater input spread to the north, while the general current flow eastward 30 °E followed in the north-west and brought the open shelf water to the research area.

As a result of the spread of the Dniester and Danube runoffs along the coast in all the surface distributions was observed the narrow coastal strip of high nutrients concentrations, with maximum at station near the Danube estuary (2 – 3 miles from the coast).

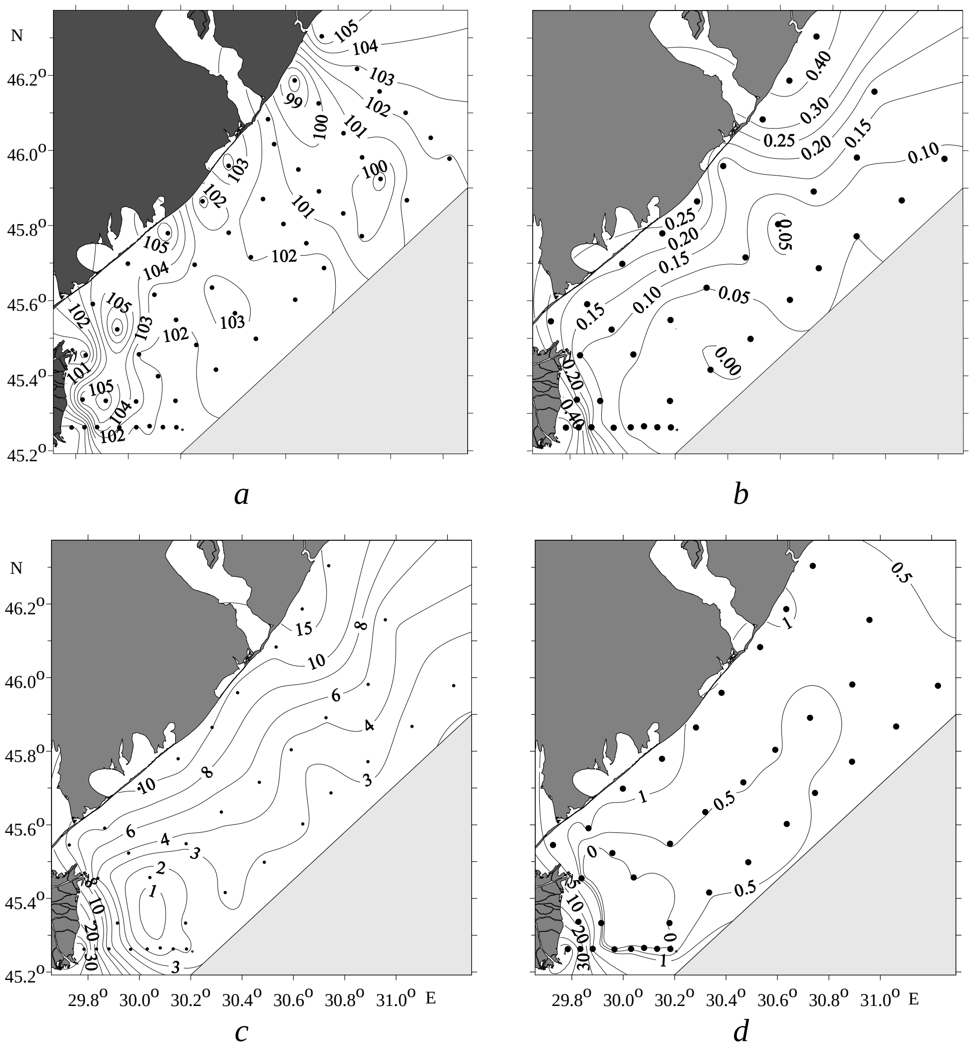


Fig. 6. Surface distributions of the (*a*) oxygen saturation (%), (*b*) phosphate, (*c*) silicate, (*d*) nitrate, all (μm) in October 2009

Maximum values fixed at the station closest to the Danube mouth were: oxygen saturation – 105 %; phosphate – 0.7 μm, silicate – 50 μm, nitrate – 50 μm, nitrite – about 1 μm. When at the distance of 10 miles away from the coast, the concentrations of all nutrients decreased at least 10 times, and the background values at 30.1 °E were respectively: 0.05 μm; 1 – 2 μm; 0.5 μm; 0.05 μm, which is about 10 – 50 times less than the maximum values.

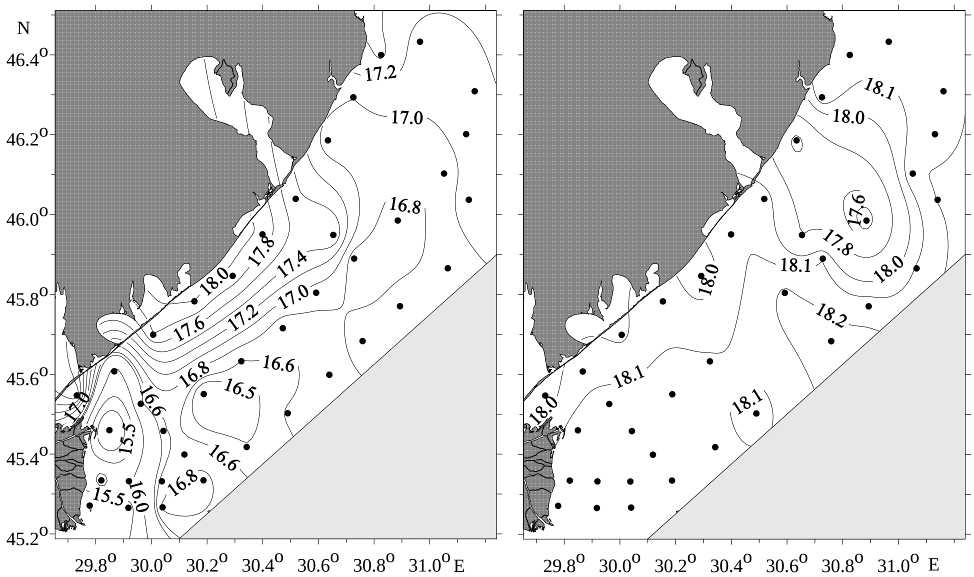
As a result of filling the research area by open shelf waters there was practically the same oxygen saturation (101 – 103 %) of the surface and near-bottom waters, only near the Danube mouth the saturation decreased to 98 % or even less. Another consequence of the Danube runoff "locking" and the north-western shelf waters "ventilation" was substantially homogeneous vertical distribution of nutrients almost everywhere, so the nutrients distribution in the surface and bottom waters to the east of 30.0 °E were very similar. The exception was the already mentioned narrow alongshore strip near the Danube mouth, where the content of nutrients at the surface, due to the content of freshwater runoff, was significantly higher than at the bottom.

Taking into the consideration the hypoxia found in this region in November 2001, the western part of section at 45 °N 10' in October 2010 was performed across every 1.5 – 2 miles, nevertheless, no expected areas with obvious oxygen deficiency have been detected. This situation, when oxygen saturation of the near-bottom waters exceeded 100 %, and besides it 100 % saturation isoline was only 2 miles away from the estuary, was rare for the coastal waters near Danube mouth. As a result, the areas with high nutrients concentrations in the near-bottom waters in the section at 45 °N 10’ were absent (no figures given).

If the seasonality is not taken into account, the distributions of nutrients in August 2009 and October 2010 supplement each other contrastively. In August the entire research area was filled with freshened waters that led to oxygen supersaturation in surface waters and the formation of hypoxia conditions at the bottom. Eventually the nutrients concentrations at the surface and at the bottom were dramatically different. Whereas in October, almost the entire research area was filled with the open shelf water, leading to homogeneous vertical distribution of the dissolved oxygen and nutrients, except the alongside strip near the Danube estuary.

September 2013. The survey of the coastal waters near Danube mouth in September 2013 was preceded by continuous northern winds that didn’t permit the Danube runoff to spread northeast and provoked the wide alongshore upwelling to the southwest of the Dniester Liman [22]. Salinity of surface waters at the stations closest to the shore (about 2 – 3 miles off the shore) was over 18 ‰, whereas at the rest of the research area it didn’t exceed 17 ‰ (this isohaline can show the size of the upwelling area) and sharply decreased approaching to the Danube mouth (Fig. 7, *a*). Almost everywhere near-bottom level was occupied by the open shelf waters with salinity over 18 ‰ (Fig. 7, *b*).

In autumn it should been expected the oxygen supersaturation of surface coastal waters rich in nutrients. However, the rise of the oxygen-depleted near-bottom waters to the surface (see information about oxygen saturation of near-bottom waters below) led to environmentally alarming situation when oxygen saturation didn’t exceed 80% in the water column of 2 – 3 mile alongshore strip to the south-west of the Dniester Liman (Fig. 8, *a*). We can assume that such upwellings, bringing to the surface oxygen-depleted near-bottom water, were the cause of fish-kills, regularly occurred in this region previously [23, 24]. One of the aforementioned upwellings had taken place recently [25].



a *b*

Fig. 7. Salinity distributions (‰) at (*a*) surface and (*b*) near-bottom in September 2013

Significantly higher nutrients concentration (compared with background values) were observed in the oxygen-depleted bottom waters of 2 – 3 mile alongshore strip which had gone up to the surface: phosphates – over 0.8 μm (when the background value in the south-east was 0.4 μm); silicate – over 15 μm (when the background 1 μm); total amount of nitrate and nitrite – over 3.5 μm (when the background 2.1 μm) (Fig. 8, *b* – *d*); ammonium – over 0.7 μm (when the background 0.2 μm). It should be also noted that the concentration of silicate to the southeast of the Dniester Liman was practically the same as the one near the Danube estuary. In the near-bottom waters from the Danube estuary to 30.3 °E the area with low oxygen water saturation (less 50 %) remained (Fig. 9, *a*). The size of this area before upwelling was undoubtedly greater; probably, the area occupied the entire research area, as in September 1997 (see above).

Concentrations of all nutrients in the area limited by isoline of 55 % oxygen saturation were significantly higher than in the eastern part of the research area: phosphate – over 0.1 μm; silicate – 10 – 15 μm; total amount of nitrate and nitrite – 4.2 – 4.8 μm (Fig. 9, *b* – *d*); ammonium – about 0.5 μm. In the near-bottom waters at eastern border of the research area a high salinity tongue (over 18.1 ‰) was observed. It marked the zone of the farthest open shelf water penetration. Oxygen saturation in this tongue was higher, up to 90 %, while nutrients concentration was less than in the waters nearby: phosphates – about 0.05 μm; silicate – about 4 μm, total amount of nitrates and nitrites – about 2.2 μm; ammonium – 0.2 μm.

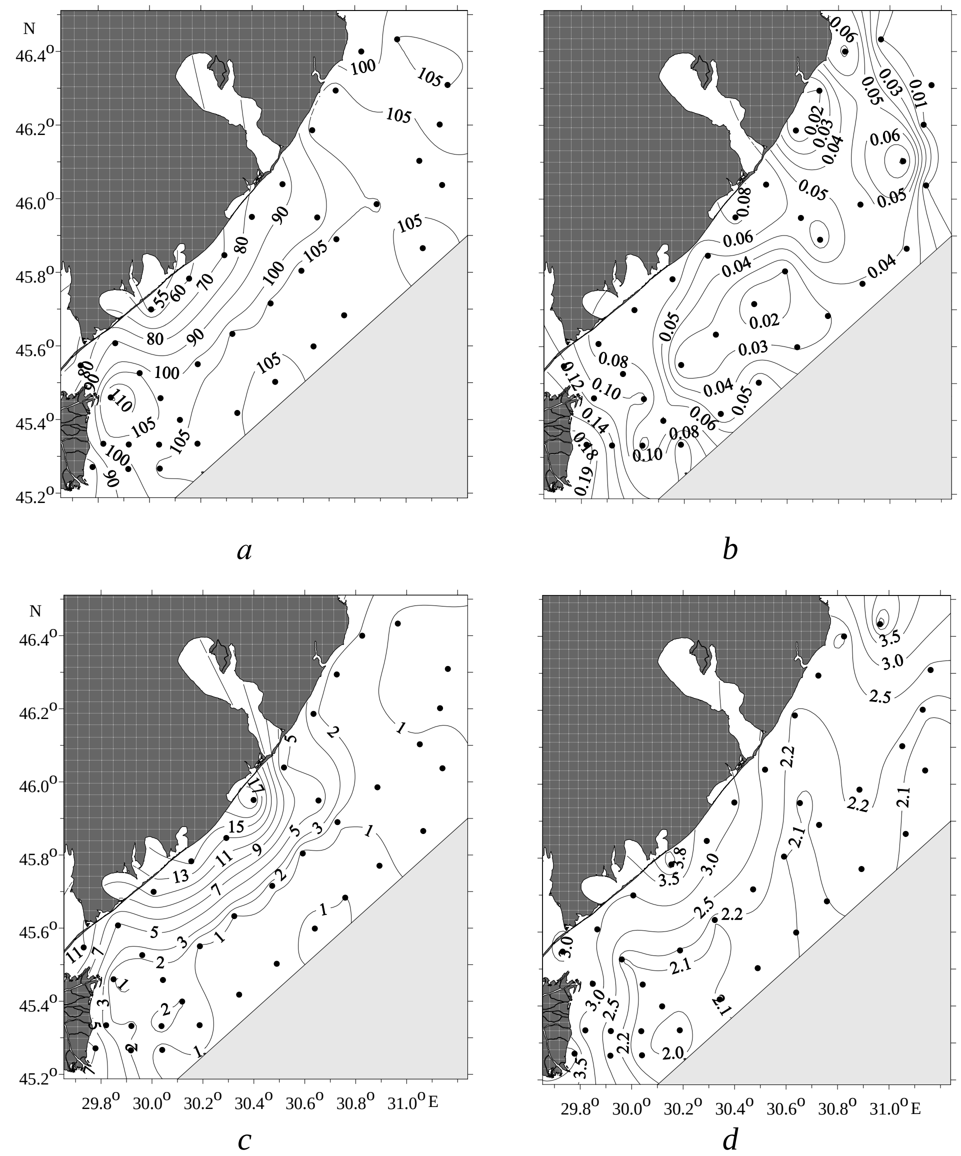


Fig. 8. Surface distributions of the (*a*) oxygen saturation (%), (*b*) phosphate, (*c*) silicate, (*d*) nitrate, all (μm) in September 2013

Thus, near the Danube estuary in three recorded cases of near-bottom waters rising on surface as a result of upwelling a significant decrease in oxygen saturation and the increase in content of nutrients in surface waters was revealed. No doubt, that the similar increase in concentration of the other decomposition products of deposited particulate organic matter (including toxic ones) should take place. Such a situation would negatively affect the state of hydrobionts, including the formation of fish-kills.

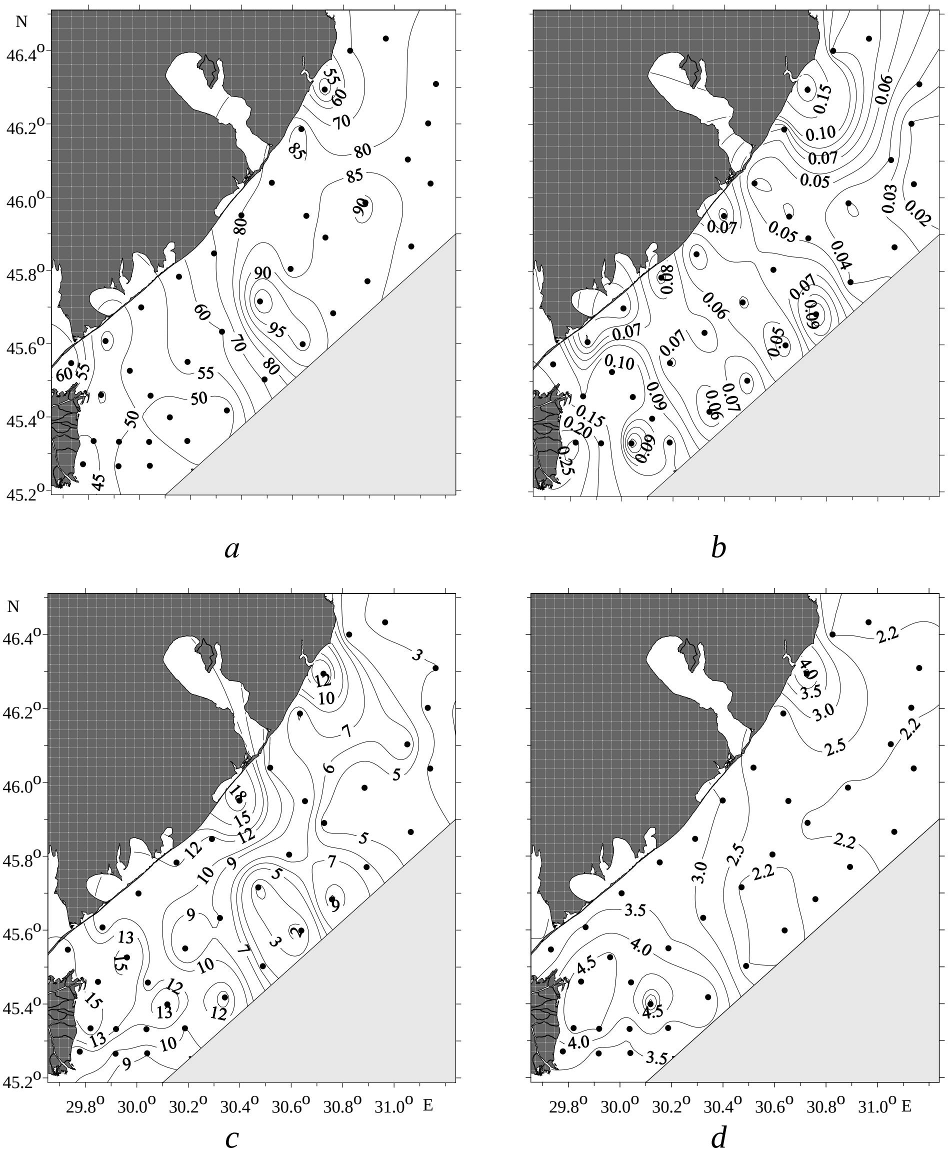


Fig. 9. Near-bottom distributions of the (*a*) oxygen saturation (%), (*b*) phosphate, (*c*) silicate, (*d*) nitrate, all (μm) in September 2013

In all the above cases, the differences in the degree of oxygen saturation had the greatest influence on the content of silicate; in some cases, the bottom hypoxia provided higher silicate concentrations in the near-bottom waters then in the estuarine surface waters. The less influenced by redox conditions was the spatial distribution of nitrite, which was not significantly different for the near-bottom and surface waters in all described cases. Perhaps this is due to the fact that the nitrite is intermediate form in the reactions of nitrification and denitrification, which maintain the same concentration level of nitrite provided that there are oxidized (nitrate) and reduced (ammonium) nitrogen forms in the water. At the same time nitrite may be consumed in the *anaerobic ammonium oxidation* reaction, when they interact with the ammonium resulting in the formation of elementary forms of nitrogen [26, 27].

Conclusion.

1. A qualitative analysis of the relationship between water oxygen saturation and the nutrient distribution in surface and near-bottom waters near the Danube estuary during various hydrological seasons was carried out. The three most important nutrient distributions were noted:

– in case the Danube runoff spreads to the East for a considerable distance (30 – 50 miles), the content of nutrients in the oxygen supersaturated surface waters is significantly lower than in the near-bottom waters with the oxygen deficit;

– in case of the Danube runoff "locking" in the narrow alongside strip and the entire estuarial area filling by open shelf waters, a substantially homogeneous vertical distribution of nutrients outside the 2 – 3 mile alongshore strip takes place;

– in case of upwelling, the risen oxygen unsaturated bottom waters propagating within 20 – 30 mile distance from the shore contain much more nutrients than the surrounding ones.

2. In case of upwelling in such hydrochemically complex area, as the coastal waters near the Danube estuary, possible sharp decrease of oxygen saturation and increased content of nutrients in surface waters may negatively affect the state of hydrobionts.

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