

# Field of the Dissolved Organic Matter Content in the Taganrog Bay (the Sea of Azov)

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Based on the actual and climatic oceanological data, the notions on composition of the field of the dissolved organic matter content in the Taganrog Bay, from the Don River mouth to the Azov Sea adjacent water areas are obtained. The features of the natural marginal filter of the Don mouth and the runoff waters in the bay are considered. Significant heterogeneity in the field of the considered characteristic (its concentration exceeds the natural standard in the Don mouth) is revealed, that can probably be a consequence of the dissolved organic matter anthropogenic sources, in other words, waste waters from the settlements. The pronounced frontal section, i. e. a natural marginal filter, was revealed in the field of the dissolved organic matter concentration. It was located along the maritime part of the Don River mouth within the narrow shore strip (its width is approximately 0.5–1.0 miles). Across this natural marginal filter, the dissolved organic matter concentration reduced abruptly towards the open sea. Up to 50% of the dissolved organic matter brought to the marine part of the Don mouth remained on the filter. It is revealed that salinity and the dissolved organic matter content in the marginal filter area are closely bound by the backward correlation dependence with the coefficient -0.87. It is shown that the dissolved organic matter concentration in the Taganrog Bay decreases in the area between the marginal filter and the runoff front from 20 to 3 mg/l, and complete transformation of the bay waters saturated with the dissolved organic matter is observed in the runoff front which, in course of the major part of a year, is located at the bay outlet. Seaward off the front external boundary (isohaline 10 PSU), the fields of salinity and dissolved organic matter content are characterized by spatial homogeneity with the 10-13 PSU salinity and the dissolved organic matter concentration 1-3 mg/l which are typical of the Azov Sea open water areas. It is found that weakly pronounced vertical stratification of the field of the dissolved organic matter concentration is peculiar to all the studied water areas.

**Keywords:** dissolved organic matter, marginal filter, runoff front, the Don River, the Taganrog Bay.

**Acknowledgements:** the research is carried out within the framework of the State Orders on the themes No. 0827-2014-0011 “Studies of regularities of the marine environment state changes based on the operational observations and the data of the nowcast, forecast and reanalysis system of the marine areas state” (code “Operational oceanography”) and № 0827-2014-0010 *Complex Interdisciplinary Research of the Oceanological Processes Determine the Functioning and Evolution of the Ecosystems of the Black and Azov Seas, based on Modern Methods for Marine Environment State and Grid Technologies* (Fundamental Oceanology code).

**For citation:** Lomakin, P. D., 2018. Field of the Dissolved Organic Matter Content in the Taganrog Bay (the Sea of Azov). *Physical Oceanography*, [e-journal] 25(6), pp. 459-471. doi:10.22449/1573-160X-2018-6-459-471

**DOI:** 10.22449/1573-160X-2018-6-459-471

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## Introduction

The main source of dissolved organic matter (DOM) in the coastal zone of the seas and oceans is associated with river runoff [1–4]. The natural content of this substance in river water varies in the range of 20–50 mg/l [5, 6], whereas in sea and ocean waters the DOM concentration is much lower. Thus, according to [7] (data of instrumental observations), in the upper layer of water in the central Black Sea, PHYSICAL OCEANOGRAPHY VOL. 25 ISS. 6 (2018) 459

the characteristic concentration of this element is about 2 mg/l. According to the estimates, approximately the same DOM concentration is peculiar to the waters of the Atlantic and Pacific Oceans. In the Baltic and Caspian seas, it varies in the range of 5–6 mg/l, and the Azov Sea waters are characterized by an increased concentration of this substance – up to 10 mg/l.

Note also that the considered parameter of the aquatic environment is one of the most effective indicators of the coastal marine water quality and is widely used in the practice of solving operational environmental problems [8, 9].

At the same time, due to the lack of mass empirical information on the DOM content in oceanographic databases, this element field in the oceans and seas is not well studied from the classical oceanography standpoint. This also applies to the Azov Sea water area. Its waters are maximally saturated with DOM, and there is no empirical information about its concentrations. At least, they are not in the database of Climatic Atlas of the Sea of Azov [10].

The present paper is aimed to identify patterns in the structure and seasonal variations of the DOM concentration field, as well as its transformation in the Taganrog Bay, from the river part of the Don delta to the open waters of the Azov Sea. A relatively small water area was studied, receiving a significant amount of this substance with runoff from the rivers flowing into the bay. Except the Don – the Kalmius, Mius and Eya rivers flow in here (Fig. 1, borrowed from [10] and adapted to the problem being solved). The natural marginal filter of the mouth area is considered. Its geometric parameters, filtration properties and thermohaline characteristics were evaluated. DOM transformation in the main arms of the Don River, on a natural marginal filter at its mouth, on the entire water area of the Taganrog Bay and on the runoff front dividing the bay and open waters of the Azov Sea. DOM fields characteristic for low water and high water periods are analyzed.

### **Initial data and methods of research**

In the situation of lack or in the absence of data of DOM field observations in the oceans and seas, the task of determining its content is greatly simplified due to the close natural statistical relationship between salinity and its concentration in unpolluted water areas [11–16]. In the proposed work for the construction of the average monthly climatic fields of DOM content, the methodical method of supplementing the missing field observations with their calculated values was used.

Since the beginning of this century, the *Kondor* optical probe [17] has been actively applied in expeditionary research of Marine Hydrophysical Institute (MHI). It permits to monitor the thermohaline characteristics with good accuracy and vertical resolution synchronously *in situ* in combination with unconventional for classical oceanography information on the concentration of total suspended and dissolved organic matter. Such probes are widely used in the world practice of oceanological and hydrological empirical research over the past 20–30 years [18–20].

DOM content was estimated by the concentration of dissolved organic carbon measured by the fluorescence method (*fDOM*) (*ex370/em460*), calibrated in *quinine sulfate equivalents* (*QSE*) standards and converted to weight units as recommended by *Water Quality Sampling and Monitoring Meters and Instruments*, and also according to the array of results of comparison with the direct method of high-

temperature catalytic combustion ( $R^2 = 0.74$ ). The obtained coefficients are used in the processing of primary information.

The relevant evidence accumulated by MHI during the expeditions to the Azov Sea (see Table) served as the basis for the commencement of an oceanological survey of the DOM field.

Table

**Data of MHI expeditionary studies in the Azov Sea, dissolved organic matter content**

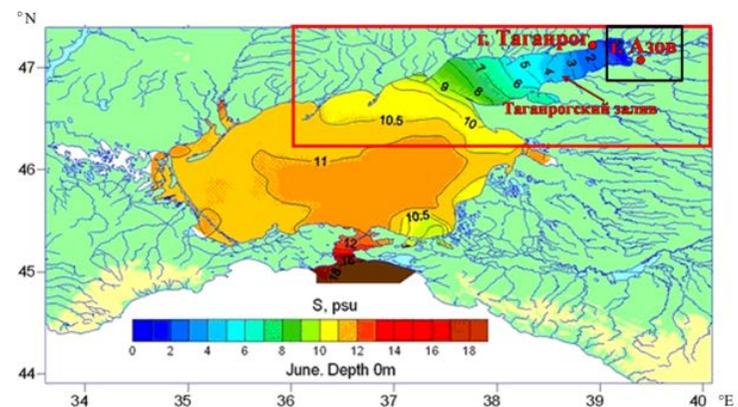
Region	Date	Quantity of Stations	DOM, mg/l
Don mouth	June, 2015	44 (river)	40–62
		11	16–42
Northern part of the sea	September, 2002 – June, 2013	37	3–22
Western part of the sea	June, 2013	13	1–3
Southern part of the sea	August, 2003 – August, 2014	59	1–3
Center of the sea	September, 2002	12	1–3
Lake Sivash	June, 2013 – October, 2016	23	1–4

Currently, the database for this element for the Azov Sea includes 199 probes that are extremely unevenly propagated throughout the water area. In particular, the information of interest is available only for the section of the Taganrog Bay, adjacent to the Don mouth. There is no such data available for the predominant part of the studied area (see Table).

The lack of relevant empirical information is compensated by applying the computational method using the simplest linear equation obtained relating the DOM concentration with the salinity in the area of the studied water area between the Don mouth and the seaward boundary of the Taganrog Bay.

The actual DOM concentration field in the Don mouth was analyzed on the basis of expedition materials conducted by MHI on June 11–15, 2015. DOM data on the seaward boundary of the Taganrog Bay were calculated using the salinity field using average monthly salinity patterns taken from the climatic atlas [10]. For this purpose, the linear regression equation is used, which relates the concentration of dissolved organic matter to salinity in the Azov Sea waters which are not affected by river runoff [16].

When interpreting the structure elements and variability of the fields of hydro-physical quantities and the DOM content field in the Don mouth, information about the synoptic situation, as well as data from the web-pages [21, 22] on the wind and sea level at two hydrometeorological posts – the Azov and Taganrog ones. The first post is located directly in the Don Delta (the southern shipping arm of the Don) and the second (marine) one – the closest to its seashore (Fig. 1).



**Fig. 1.** Water area under study (in the red frame) and the MHI survey polygon in the Don River mouth (in the black frame) on the salinity climatic map of the Azov Sea surface in June [10]

### Discussion of the results

The most significant factors determining the water dynamics and significantly deforming the structure of the fields of hydrophysical, hydrochemical and hydrobiological elements in the Don Delta are due to wind and surge processes, which are well studied and described in the survey area and scientific literature [23–26]. Particularly, it is known that in the Taganrog Bay and the eastern Azov Sea, the eastern component winds cause negative water surge, the western component ones – the positive surge and, accordingly, the characteristic water circulation in the bay and the Don Delta.

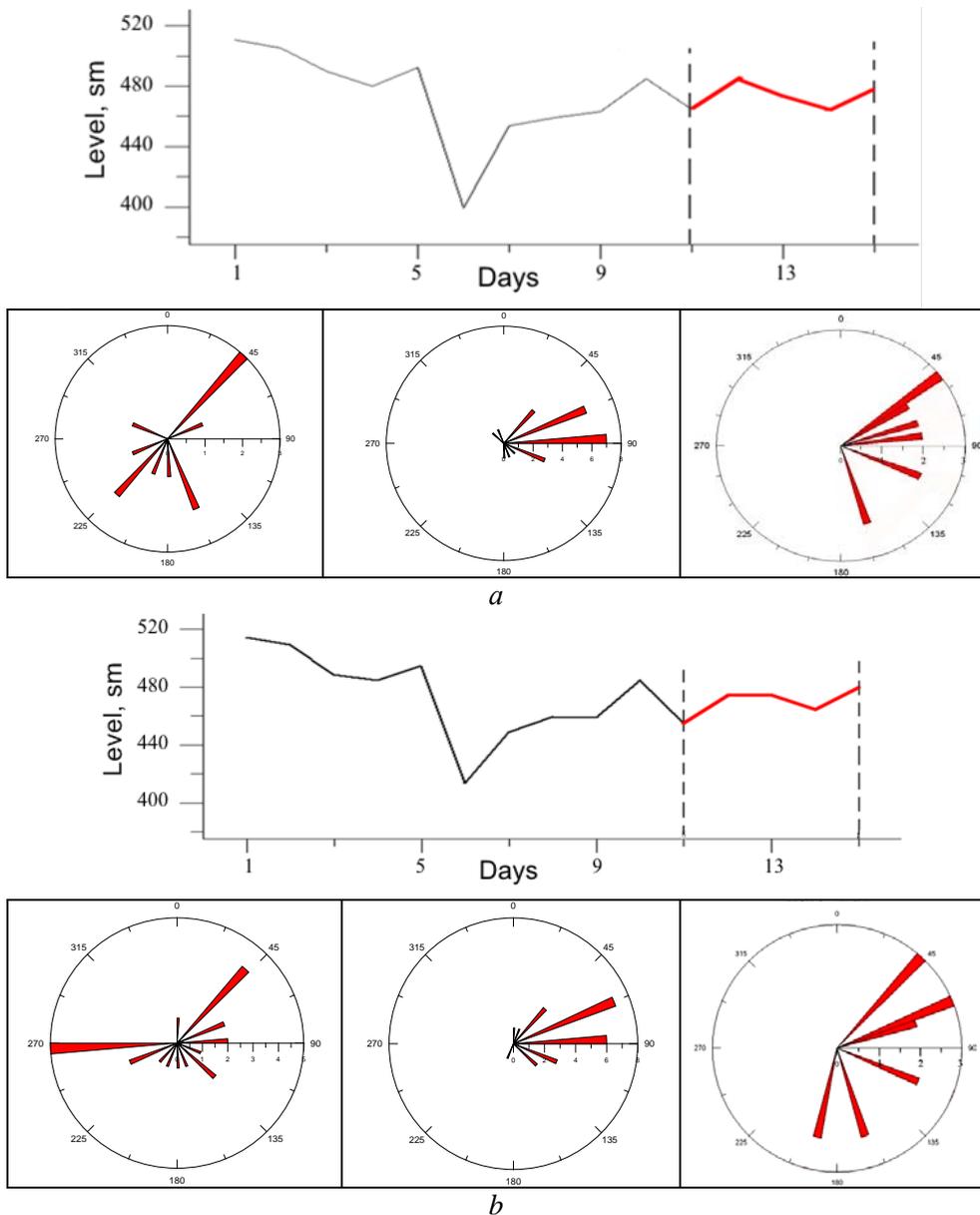
I. e., the analyzed data of the expedition to the mouth of the Don, as well as any other actual oceanological information relating to the considered region contain a synoptic component. Therefore, if it is significant, this data cannot be combined with climatic average monthly values, in the arrays of which this component is filtered by the averaging operation.

To assess the wind component significance, the analysis of fluctuations and shape of the level surface in the Taganrog Bay, depending on the synoptic atmospheric situation and wind before and during the survey in the Don Delta, is presented below.

At the end of May 2015, the weather in the region was determined by the front of a filled cyclone centered over the north of Ukraine. Moderate and strong surge of south-westerly winds with a velocity of 6–11 m/s, which were observed on May 29 and 30, promoted the water surface level elevation on the shore and in the arms of the Don Delta to 534 and 536 cm, respectively (Fig. 2).

In the first three days of June, there was a change in the natural synoptic process, accompanied by the wind vector reversal to the northeast. The effect of the eastern periphery of the Azores maximum crest spread over the studied water area. It caused eastern moderate quarter winds with a speed of 3–7 m/s and a noticeable drop in water level to the minimum marks – 381 cm in the Taganrog post and 396 cm in the Azov post – on June 6. Then, under the same synoptic situation, but due to a decrease in the horizontal pressure gradient in the region, the weather was established with a weak (1–3 m/s) wind of the eastern quarter alternating with wind-

less conditions. As a result, the surge effect disappeared, and the water level in both points rose to 494 and 499 cm on June 6–10 and later was in a stable state. During the survey at both points, it almost synchronously fluctuated relative to these marks with a small daily span, decreasing in time from 25 to 10 cm.

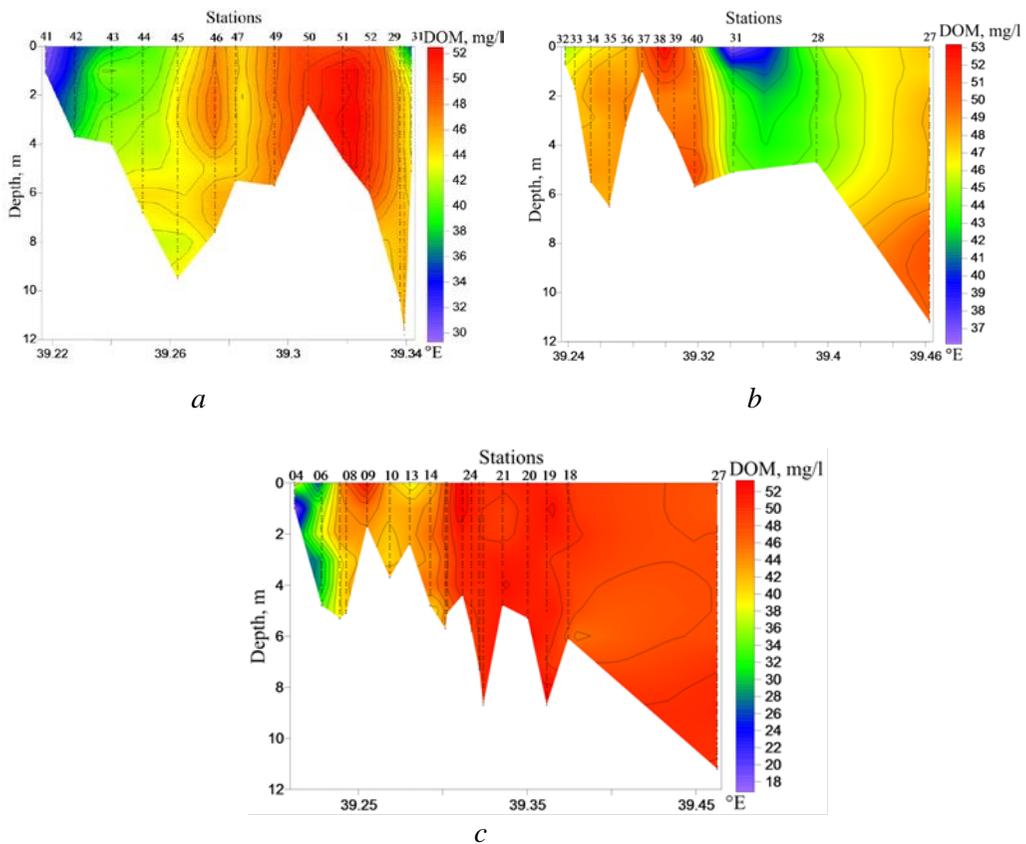


**Fig. 2.** Sea level variation based on the Taganrog hydrometeorological station data and wind roses corresponding to its basic phases in June, 2015 – (a); the same characteristics for the Don branch based on the Azov hydrometeorological station data (b)

The survey was carried out in the conditions of the prevailing southeastern wind with a speed of 2–4 m/s (Fig. 2). At its beginning (June 11 and 12), the mean daily sea level in the Taganrog post exceeded the level in the Azov one by 10–11 cm. Over time, the level surface slope changed to the opposite one. In the second half of the survey, June 13–15, the average daily sea level in the Taganrog post was 1–2 cm below the level in the Azov post.

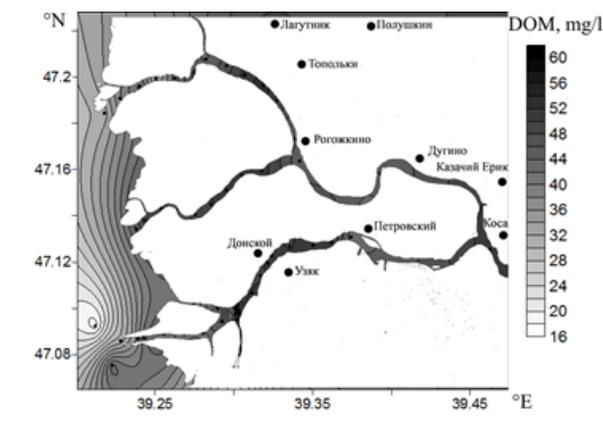
That is, during the survey, the level surface shape in the Don Delta and in the Taganrog Bay was close to horizontal and slightly distorted in time. This indicates the almost complete absence of a component in the fields, which was determined by the wind surge effect, and that the actual oceanographic fields observed during the expedition were close to the climatic average monthly distributions for June.

The DOM concentration field in the river branches and on the Don shore was characterized by the following main properties. River waters varied in relative uniformity in the vertical. At the parts remote from the mouth, they were poorly stratified. A small vertical gradient of a different sign in separate layers as a result of the interaction of river waters with the waters of the seashore is marked on the approach to the sea at a distance of 1–2 miles. At the seashore, the concentration of the studied element field slightly changed with depth (Fig. 3).



**Fig. 3.** Dissolved organic matter (DOM) vertical distribution in the Don mouth on June 11–15, 2015: *a, b* – in the canals of the unnavigable branch Kalancha; *c* – in the navigable branch Don

In the horizontal plane, noticeable inhomogeneities were detected in the DOM content field. Significant changes in this substance concentration, 40–62 mg/l, are monitored along the river streamways. Separate water lenses saturated with DOM to more than 50 mg/l (maximum natural rate) are a likely consequence of the presence of anthropogenic sources of this substance within the water area under study. This may be the wastewaters located in the Don delta settlements (Fig. 3, 4).



**Fig. 4.** Dissolved organic matter content (mg/l) in the near-bottom layer of the Don River mouth on June 11–15, 2015

Similar situations (according to the materials of MHI expeditions) are observed, for example, in the Dnieper-Bug estuary and in the coastal waters of Crimea, where water areas near all settlements without exception and even individual sanatorium buildings and other objects of economic activity are characterized by the presence of local maximums of DOM content exceeding the natural the norm.

The horizontal structure of the DOM concentration field at the seashore was characterized by the presence of a pronounced meridionally oriented front in the entire water column (Fig. 4).

Along the shoreline of the Don mouth area in a narrow riverside about 0.5–1.0 miles wide, the DOM concentration sharply decreased towards the open sea from 35–42 mg/l to minimum values 16–20 mg/l. The horizontal gradient of the content of this substance on the frontal section reached 20–30 mg/l per mile. The front in the DOM field was located in fresh water. Salinity (mineralization) within its range increased towards the sea from 0.6 to 1.0 PSU. The temperature decreased in the same direction from 26.6 to 24.2 °C.

Similar frontal formations observed in river mouths are called natural marginal filters. Studies carried out based on a physical model, as well as field observations [15, 27 and 28], revealed that in the marginal filters of the oceans and seas, in the mouths of such great rivers as the Amazon, Lena, Yenisei, Ob, up to 90–95 % of suspended and 30–40 % of dissolved substances and pollutants of the river runoff remains.

Judging by the difference in the DOM concentration at the filter boundaries, in the case under consideration up to 50 % of the dissolved organic substances contained in the river water in the lower Don were retained on it (Fig. 4).

It should be noted the following interesting feature. In the northern and southern branches of the Don Delta at a distance of about 2–3 miles to the shore, the DOM concentration noticeably dropped from 60 to 40 mg/l (Fig. 4). That is, the filtration mechanisms worked both on the seashore and in the river beds, and about a third of the total amount of dissolved organic matter, which was contained in the upper part of the river delta, remained in the river section of the filter.

In [15, 27 and 28], it was shown that the natural marginal filters of rivers flowing into the seas and oceans are characterized by a close inverse correlation between the DOM content and the salinity of the water with a high coefficient of about  $-0.90$ . A similar property is revealed for the marginal filter the Don. In our case, the correlation coefficient between the corresponding values turned out to be  $-0.87$ .

The aforementioned result shows that the actual situation considered (Fig. 3 and 4) reflects the real DOM concentration field with its structural elements typical of the Don Delta in June. The isohaline  $S = 1$  PSU, which coincides with the isoline of the DOM concentration equal to 20 mg/l, can be conditionally taken as the seaward boundary of this part of the Taganrog Bay. From this conditional boundary, the DOM concentration in the Taganrog Bay, as the salinity increases, decreases to 1–3 mg/l towards the Azov Sea open waters (see Table).

According to the classic oceanological concepts [29], the complete transformation of the properties of the waters of the rivers flowing into the oceans and seas occurs on their drainage haline (thermohaline) fronts.

The runoff haline front in the actual salinity fields during most of the year is located at the outlet from the Taganrog Bay. It approximately coincides with the western geographic boundary of the bay, a meridionally oriented conditional line, passing along the Dolgaya and Belosarayskaya Spits. In the spring, during a flood, the front shifts in a western southwestern direction [30]. Climate data determine a similar position of the front [10]. At the same time, it should be noted that over the past few years a significant increase in salinity in the Taganrog Bay to 14 PSU and a corresponding displacement of the runoff front to the east, to its inner area, was recorded.

According to the monthly average salinity climatic fields [10], it is easy to determine the seaward boundary of the front under consideration throughout the year. It coincides with the position of the 10 PSU isochaline, beyond which the haline field in the central Azov Sea and on its western and southern shores becomes more homogeneous in horizontal terms, and the salinity varies within 10–13 PSU (Fig. 1).

Based on the linear regression equation [16], relating the DOM content with the salinity  $S$  in the Azov Sea waters

$$\text{DOM} = 30.87 - 2.78 S, \quad (1)$$

the correlation coefficient  $R_{S/\text{DOM}} = -0.80$ , it is possible to determine the concentration of this substance on the seaward front boundary – 10 PSU isohaline, as well as to evaluate the filtration properties of the runoff front of the Don. An elementary calculation shows that on the seaward boundary of the considered runoff front, the DOM concentration in its climatic field decreases to 3.07 mg/l.

Taking into account that the characteristic DOM concentration in the sea center is 1–3 mg/l [16], then it can be argued that almost all the dissolved organic matter that falls into the Taganrog Bay with river runoff accumulates on the front under consideration.

It is shown above that on the eastern natural border of the Taganrog Bay (marginal filter) the 1 PSU salinity corresponds to DOM concentration of 20 mg/l; on the western boundary of the runoff salinity front at 10 PSU corresponds to a DOM concentration of 3 mg/l. This data make it easy to obtain a linear equation that relates the analyzed values of the studied mean monthly June fields in the designated area:

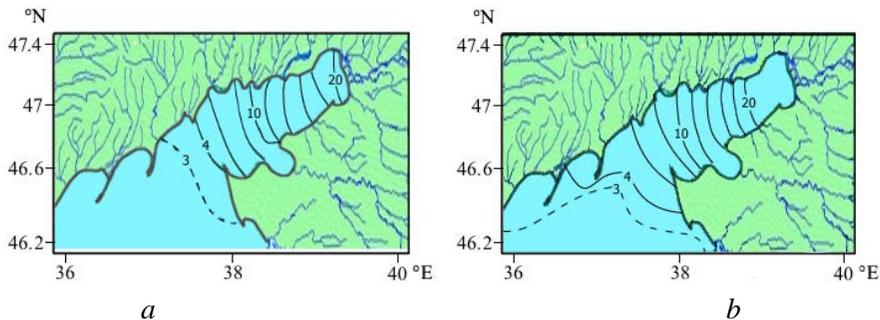
$$\text{DOM} = 21.9 - 1.9 S. \quad (2).$$

Equation (2) permits to calculate the horizontal mean monthly distribution of DOM concentration by the mean monthly salinity field in the Taganrog Bay [10].

Seaward boundary of the runoff front for all months of the year is represented by 10 PSU isochaline and, according to (1), the DOM content is 3 mg/l. Supposing that the DOM and salinity concentration on a marginal filter in the Don mouth do not experience significant changes during the year, then equation (2) can be used to calculate the climatic field of DOM content in other calendar months of the year.

Since in the uncontaminated waters of the Azov Sea the field of concentration of the studied value is weakly stratified in depth, all information about its structure is contained in surface distributions.

Fig. 5 shows the horizontal distributions of DOM concentrations in the Taganrog Bay in June and March, obtained by a calculation method based on the above equation (2) and the mean monthly salinity distributions on the Azov Sea surface [10].



**Fig. 5.** Dissolved organic matter content (mg/l) on the Taganrog Bay surface: *a* – in June, *b* – in March

The concentration field in Fig. 5, *a* is typical for the summer months when there is a minimum DOM amount in the low-water periods under a minimum runoff of the rivers in the waters of the bay. In early spring, during the flood (Fig. 5, *b*), the amount of dissolved organic matter of terrigenous nature in the studied region is maximum. At this time, the water area with the maximum terrigenous component of the DOM significantly expands. Its natural boundaries is the marginal filter and the runoff front shift toward the open part of the sea.

During the flood, compared with the situation observed during low water periods, the area of the water with a maximum (20–40 mg/l) DOM content in the marine part of the Don Delta increases by 4–5 times. Due to the inflow of water from the Taganrog Bay, the DOM concentration in the northeast and north of the Azov Sea increases by 1–2 mg/l.

Recall that until recently, the DOM content field in the Azov Sea seemed homogeneous with a constant concentration of 10 mg/l.

The fields shown in Fig. 5 concern the region with the maximum DOM content in the Azov Sea. This is the Taganrog Bay, where the concentration of this substance varies from 40 mg/l in the mouth area of the Don to 3 mg/l in open waters. In the predominant part of the sea, the DOM content is dozens of times less. This indicates a significant heterogeneity of the field of the considered parameter of the Azov Sea aquatic environment.

The revealed structure patterns relate to the mean monthly fields, whereas the actual DOM field in the Taganrog Bay is much more complicated. Apparently, it is also subjected to significant temporal variability and requires further research, first – at the empirical level.

### **Conclusion**

On the basis of mean monthly salinity fields, computational methods and actual data on observations of DOM content, diagrams of horizontal distribution of this substance were obtained and regularities of the structure of its field in the Taganrog Bay waters were revealed, from the Don mouth to the adjacent waters of the Azov Sea. The properties of the natural marginal filter of the mouth area and the runoff front of the bay are considered. Seasonal variations of the concentration field of the studied element of the aquatic environment are analyzed.

It is shown that in the river branches and on the Don Delta side the vertical stratification of the DOM concentration is poorly pronounced. Significant heterogeneity in the field of the content of the considered characteristic with a concentration exceeding the natural norm found in the river waters is a likely consequence of anthropogenic sources of this substance associated with the wastewater of human settlements.

Along the seaward part of the Don mouth region in a narrow riverside about 0.5–1.0 miles wide at a salinity of 0.6–1.0 PSU and a water temperature of 24.2–26.6 °C, a clearly marked frontal section was revealed in the DOM field – the natural marginal filter. Across the formation, the DOM concentration dropped sharply towards the open sea from approximately from 40 to 20 mg/l. The horizontal gradient of DOM content on the front section of the filter reached 20–30 mg/l per mile. Up to 50 % of dissolved organic matter entering the marine area of the Don Delta remained in it.

In the Don Delta branches, at a distance of about 2–3 miles to the riverside, active DOM subsidence is noted. About a third of the total amount of dissolved organic matter that contained in the upper part of the river delta remained here.

It was revealed that the water salinity and the DOM content in the marginal filter area in the Don Delta are associated with a close inverse correlation with the coefficient  $-0.87$ .

In the Taganrog Bay, the DOM concentration decreased westward to the outer boundary of the runoff front from 20 to 3 mg/l, more seaward than the natural marginal filter.

The complete transformation of the DOM saturated Taganrog Bay waters is observed on the runoff front, which for most of the year is located in the climatic salinity field at the bay outlet. Spatial uniformity with salinity of 10–13 PSU and a DOM concentration of 1–3 mg/l PSU peculiar for the Azov Sea open waters).

An analysis of the DOM concentration fields for June (low water period) and March (flood) showed their significant intra-annual variability due to seasonal runoff variations of the rivers flowing into the Taganrog Bay.

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*The author has read and approved the final manuscript.*

*The author declares that he has no conflict of interest.*