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The Field of Colored Dissolved Organic Matter Content and its Relationship with Salinity in the Open Azov Sea Water

P. D. Lomakin *, D. D. Zavyalov

Marine Hydrophysical Institute of RAS, Sevastopol, Russian Federation
* *e-mail: p_lomakin@mail.ru*

Abstract
Based on the materials of a series of expeditions carried out by Marine Hydrophysical Institute (Sevastopol) and Southern Scientific Research Institute of Marine Fisheries and Oceanography (Kerch) during 2002–2013, a regression equation was obtained indicating the presence of a fairly close inverse correlation relationship between salinity and the concentration of colored dissolved organic matter in the open waters of the Sea of Azov. It is shown that the closeness of the correlation dependence between these values depends significantly on the presence of dissolved organic matter of anthropogenic origin in the waters of the studied region. Using this equation, according to the known average monthly salinity fields, the concentration fields of colored dissolved organic matter were calculated and the regularities of their structure and intra-annual variability were analyzed. It is found that the field of the studied matter is characterized by low concentration and relative homogeneity. In the open water area of the sea, salinity variations determined by the intra-annual variation in the runoff volume of the Don and Kuban Rivers do not significantly affect the spatiotemporal variability in the field of colored dissolved organic matter. It is shown that a close inverse correlation between the content of colored dissolved organic matter and salinity is an indicator of the good quality of water. A weak or positive correlation between these quantities is a sign of the presence of dissolved organic substances of anthropogenic nature in the aquatic environment.

Keywords: colored dissolved organic matter, salinity, correlation, pollution, Sea of Azov

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Поле концентрации окрашенного растворенного органического вещества и его связь с соленостью в открытых водах Азовского моря

П. Д. Ломакин *, Д. Д. Завьялов

Морской гидрофизический институт РАН, Севастополь, Россия
** e-mail: p_lomakin@mail.ru*

Аннотация
На основе материалов серии экспедиций, проведенных Морским гидрофизическим институтом (г. Севастополь) и Южным научно-исследовательским институтом морского рыбного хозяйства и океанографии (г. Керчь) в 2002–2013 гг., получено уравнение регрессии, свидетельствующее о наличии достаточно тесной обратной корреляционной связи между соленостью и концентрацией окрашенного растворенного органического вещества в открытых водах Азовского моря. Показано, что теснота корреляционной зависимости между этими величинами существенным образом зависит от наличия в водах рассматриваемого региона растворенной органики антропогенного происхождения. При помощи данного уравнения по известным полям средней месячной солености рассчитаны поля концентрации окрашенного растворенного органического вещества, проанализирована их структура и внутригодовая изменчивость. Выявлено, что поле исследуемого вещества характеризуется низкой концентрацией и однородностью. В открытой акватории моря вариации солености, определяемые внутригодовым ходом объема стока рек Дон и Кубань, не оказывают существенного влияния на пространственно-временную изменчивость поля окрашенного растворенного органического вещества. Показано, что тесная обратная корреляционная связь между содержанием окрашенного растворенного органического вещества и соленостью – индикатор хорошего качества вод. Слабая или положительная корреляционная зависимость между этими величинами – признак наличия в водной среде растворенных органических веществ антропогенной природы.

Ключевые слова: окрашенное растворенное органическое вещество, соленость, корреляция, загрязнение, Азовское море

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Introduction

The content of the dissolved organic carbon (DOC) and the colored dissolved organic matter (fDOM) are regarded as the main representative indicators of the dissolved organic matter content in sea water [1]. On the shelf of the oceans and seas, which are desalinated by river waters, in the areas of runoff fronts and frontal zones, the concentration fields of each of these indicators are associated with the salinity by a close inverse correlation with the correlation coefficient up to –0.95 [2, 3]. This correlation is due to the high concentration of the dissolved organic matter of terrigenous origin in the coastal waters, desalinated by mainland waters.

The content of this matter reduces abruptly in river mouths on a natural marginal filter and then falls noticeably at the limit of the runoff frontal zones [4, 5].

Outside coastal runoff frontal zones in the open waters of oceans and seas, such relationships and their properties are less studied. Thus, in the article [6], an inverse dependence of the concentration of dissolved organic carbon on salinity, DOC(S), was found in the open part of the Black Sea in the vertical structure of waters. This correlation, analyzed at a qualitative level by the authors of the cited work, was used by them to interpret biochemical processes in the deep-sea zone.

Note that the relationship between the indicators of the dissolved organic matter content and salinity is important and useful in a number of applied and theoretical areas of oceanology. For example, they enable us to get an idea of the structure of a poorly studied field of the dissolved organic matter content based on salinity arrays, as well as to track the trajectories of river water distribution on shelves and beyond.

The purposes of this article:

– to obtain an equation for the correlation dependence of fDOM concentration on salinity in the waters of the Sea of Azov, which are located outside the main runoff frontal zones and are not directly affected by river runoff;

– based on this equation and the known average monthly salinity fields, to calculate the content fields of the considered quantity, to identify the features of their structure and intra-annual variability;

– to evaluate the influence of the anthropogenic component of the fDOM content field on the tightness of the correlation dependence of this substance's concentration on salinity.

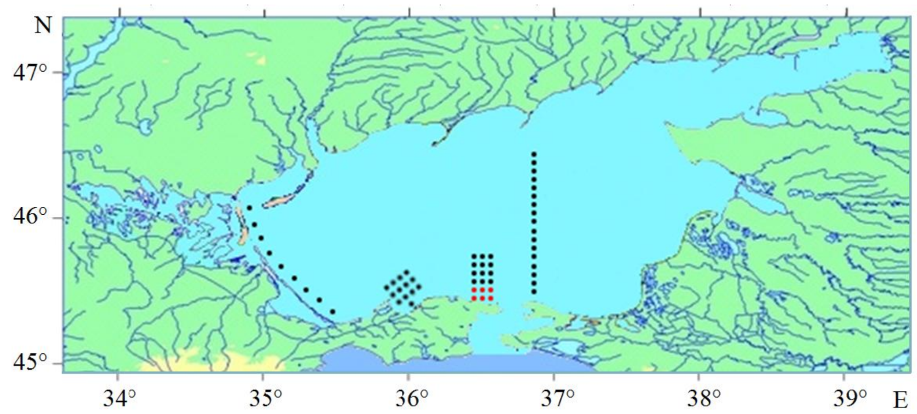
Initial data and research methods

The water area under consideration is a part of the sea characterized by maximum salinity, which includes open waters, as well as waters of the western and southern coastal areas, where the average monthly salinity is more than 10. According to the atlas[1)], isohaline 10 is a limit of coastal runoff haline zones observed along the northern and eastern coasts of the Sea of Azov and in Taganrog Bay.

The quantity under study is the optical indicator of the content of dissolved organic matter, fDOM. Its dimension is presented in optical calibration units – quinine sulfate (quinine sulfate unit, QSU) [7].

The empirical material used for the analysis is a sample of instrumental synchronous observations of salinity and fDOM concentration (54 soundings in total). They were carried out in a number of expeditions of Marine Hydrophysical Institute (Sevastopol) and Southern Research Institute of Marine Fisheries and Oceanography

[1)] NOAA, 2006. *Climatic Atlas of the Sea of Azov 2006*. International Ocean Atlas and Informational Series, Vol. 10. Available at: https://www.nodc.noaa.gov/OC5/AZOV2006/start.html [Accessed: 12 March 2023].



F i g . 1 . Map of stations with simultaneous registration of fDOM concentration and salinity (2002–2013)

(Kerch) over the time interval from 2002 to 2013. The observations covered the central, western, and southwestern parts of the sea and the region of the Kerch pre-strait region (Fig. 1).

All analysed data were obtained using the Kondor portable optical sounding complex (ecodevice.com.ru/ecodevice-catalogue/multiturbidimeter-kondor). At each sounding with a depth step of 0.1 m, the salinity and fDOM concentration were recorded synchronously *in situ*. The error of salinity measurements was ±0.01 PSU. The measurement error of fDOM content was ±0.2 QSU. The range of studied depths was 1.5–10.5 m.

The relationship between salinity and fDOM concentration was calculated using the pair correlation method. Using the resulting regression equation, the average monthly climatic fields of salinity for the considered area of the Sea of Azov [1)], which were built on representative samples of actual data, were digitized and then recalculated into concentration fields of the studied quantity.

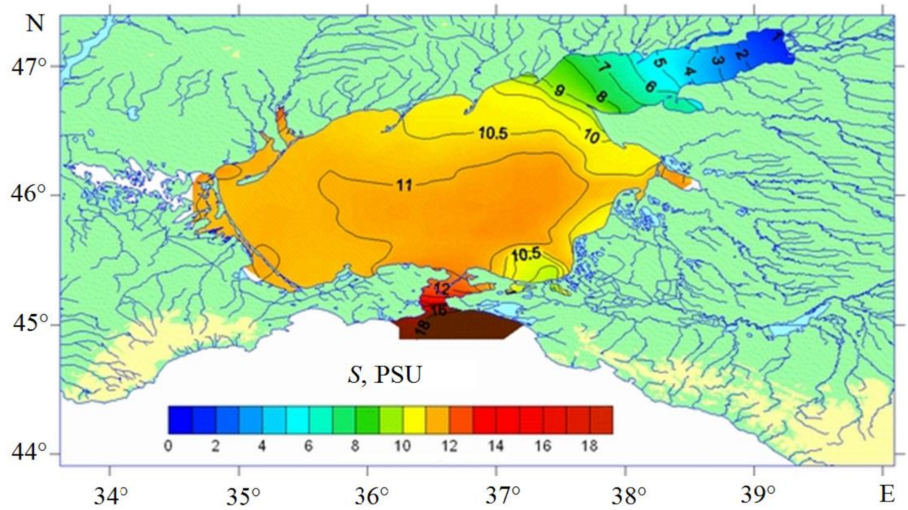
As an example, Fig. 2 shows the average monthly salinity field for June.

Discussion of the results

In Fig. 3, *a* in the S,fDOM coordinate system, the original data sample and the chart of the correlation between the analyzed quantities are shown, which implies that they are independent (correlation coefficient R = –0.14).

In the upper right corner of the coordinate plane, there is a separate cloud of points that clearly do not fit into the main field, illustrating the tendency for the fDOM concentration to decrease with increasing salinity.

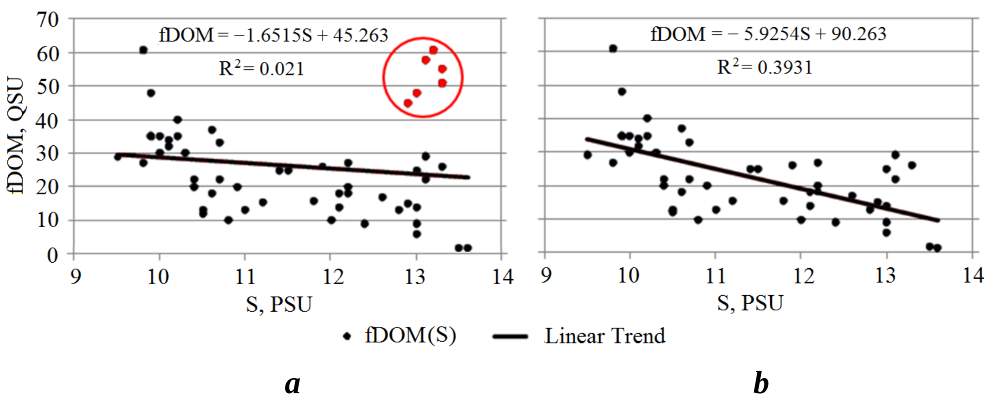
It turned out that the singular points (there are six in total), which were distinguished by the maximum concentration of fDOM (45–61 QSU) and high salinity (12.9–13.3 PSU) (circled in Fig. 3), corresponded to the stations located in the area of wastewater discharge of the Bondarenkovo Treatment Facilities in the city of Kerch (red dots in Fig. 1). These data characterized coastal waters polluted by sewage runoff and were excluded from the original sample.



F i g . 2 . Average monthly salinity in the surface layer (0 m) of the Sea of Azov in June [1)]

Based on the filtered sample, a typical inverse and rather close correlation was found between the studied quantities, correlation coefficient R = –0.63 (regression equation fDOM = –5.92·S + 90.26; N = 48 (Fig. 3, *b*)).

The result shown in Fig. 3 indicates the following. The dependence fDOM(S) responds to the presence of dissolved organic matter of anthropogenic origin in the studied waters and is a good indicator of the pollution of the aquatic environment by this substance. A close inverse correlation dependence fDOM(S) and, accordingly, a sufficiently high (in modulus) correlation coefficient are indicators of good water quality.



F i g . 3 . fDOM(S) correlation dependence charts for the studied water area of the Sea of Azov: *a* – original sample; *b* – filtered sample

A weak negative or positive correlation between the analyzed quantities is a sign of the presence of dissolved organic substances of an anthropogenic nature in the aquatic environment.

Let us consider the factors that determine the structural features and temporal variability of salinity and fDOM in the Sea of Azov.

The main factor that determines the salinity regime of the predominant part of the sea area and, accordingly, the structure and intra-annual variability of the salinity and concentration fDOM fields, is related to the runoff volume of the Don River. The maximum runoff of this river is observed in May. In the remaining months of the year, the hydrological regime of the Don is characterized by a low water period [2)].

In the eastern coastal region of the Sea of Azov, the salinity field [1)] is determined by the runoff of the Kuban River, which reaches maximum values in the summer months during intense floods due to snowmelt in the Caucasus Mountains [8].

Accordingly, the maximum desalination of the predominant part of the sea area, characterized by an average monthly salinity of 11–11.5 PSU in the central part, is observed in May and June (Fig. 2). In the remaining months of the year, the salinity of the waters of the study area is 11.5–12.5 PSU [1)] and varies slightly with time [8].

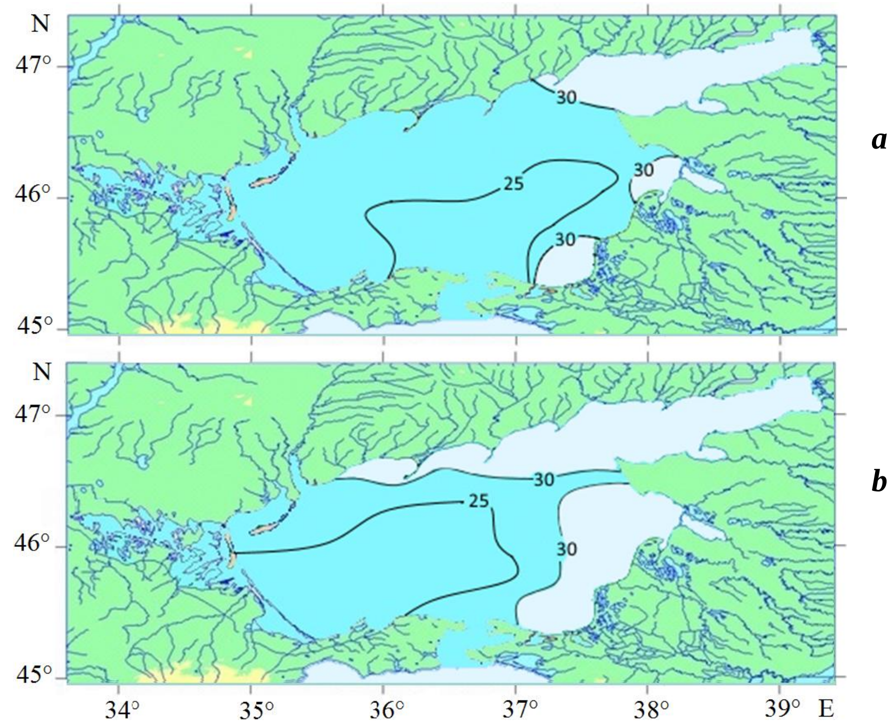
In the considered area of the sea, the average monthly salinity fields in the surface layer are uniform. The difference in salinity at the boundaries is 1.5–2.5 PSU. Also, the range of the intra-annual variation of the average monthly salinity is estimated with a small interval of 0.5–0.7 PSU.

Fig. 4 shows the fDOM distributions calculated by us on the basis of the obtained regression equation fDOM(S) and average monthly salinity fields [1)] for March and June to illustrate the features of the structure and intra-annual variability of the characteristics of the field of the studied quantity.

It can be seen that in the months related to the extreme phases of intra-annual variations in the runoff of the Don River, which determines the maximum range of intra-annual fluctuations in water salinity in the Sea of Azov, the structure of the fDOM content field in the considered water area changes insignificantly. It is homogeneous. The concentration of the analyzed substance is almost unaffected by intra-annual variations; it is minimal over the entire area of the sea and varies in the range of 25–30 QSU. According to [9], the concentration of fDOM in the waters of Taganrog Bay, in the northern and eastern desalinated coastal areas of the Sea of Azov, is maximum and varies in the range of 30–300 QSU.

The area of the areal of the minimum concentration of the considered quantity undergoes significant changes during the year. In July–March, during the low water period of the Don and the Kuban, under conditions of minimal sea desalination, it is the largest and equals 70–80% of the area of the entire sea (Fig. 4, *a*). In May–June, during floods in the Don and the Kuban, the area occupied by waters with a minimum content of fDOM is the smallest – 50–60% of the area of the entire water body of the Sea of Azov (Fig. 4, *b*).

[2)] Rodionov, N.A., 1958. [*Hydrology of the Mouth Area of the Don*]. Leningrad: Gidrometeoizdat, 95 p. (in Russian).



F i g . 4 . Concentration of fDOM, QSU, at the surface in the open part of the Sea of Azov in March (*a*) and June (*b*)

Stability of the fDOM field structure and significant intra-annual fluctuations in the area of distribution of the waters of maximum salinity can be explained as follows. According to the classical ideas of K.N. Fedorov [5], there is an abrupt change in the properties of desalinated waters at the limit of the runoff frontal zones. The influence of these waters becomes insignificant and disappears in the open sea.

The sharply increasing runoff of the Don and the Kuban is accompanied by desalination of coastal waters and inflow of a large amount of fDOM, which is mainly concentrated within the runoff frontal zone. A small proportion of this substance penetrates into the open part of the sea. During the flood, the area of the runoff zone increases, and, accordingly, the area of the Sea of Azov with maximum salinity decreases.

Conclusion

Based on the materials of a series of expeditions carried out in 2002–2013, a rather close inverse correlation was revealed between salinity and fDOM concentration (coefficient R = –0.63) in the open waters of the Sea of Azov and in the water area adjacent to its western and southern coasts.

It has been established that the correlation fDOM(S) responds to the presence of dissolved organic matter of anthropogenic origin in the studied waters and is a good indicator of the pollution of the aquatic environment by this substance. A close inverse correlation fDOM(S) is an indicator of good water quality. A weak or positive correlation between the considered quantities is a sign of the presence of dissolved organic substances of an anthropogenic nature.

Using the obtained regression equation, the fDOM content fields were calculated and plotted using average monthly salinity maps.

It is shown that in the waters of the salinized part of the Sea of Azov, due to the insignificant spatial and temporal variability of salinity, the average monthly fDOM fields are uniform and change little over time. They are characterized by a low concentration of 25–30 QSU and hardly react to sea desalination caused by the intra-annual variability in the runoff volume of the Don and the Kuban rivers. During floods on these rivers in May–June, the area of the water body with low fDOM content is minimal and occupies 50–60% of the entire area of the Sea of Azov. At all other times, during low water periods in the Don and the Kuban, it increases to 70–80 %.

REFERENCES

1. Agatova, A.I., Lapina, N.M. and Torgunova, N.I., 2018. Features of the Distribution of Organic Matter in the Waters of the Black Sea. In: A. P. Lisitsyn, ed., 2018. *The Black Sea System*. Moscow: Nauchny Mir, pp. 146–170. doi:10.29006/978-5-91522-473-4.2018 (in Russian).

2. Pugach, S.P. and Pipko, I.I., 2012. [Dynamics of Dissolved Coloured Organic Matter on the East Siberian Sea Shelf]. *Doklady Akademii Nauk*, 447(6), pp. 671–674 (in Russian).

3. Kari, E., Merkouriadi, I., Walve, J., Leppäranta, M. and Kratzer, S., 2018. Development of Under-Ice Stratification in Himmerfjärden Bay, North-Western Baltic Proper, and their Effect on the Phytoplankton Spring Bloom. *Journal of Marine Systems*, 186, pp. 85–95. doi:10.1016/j.jmarsys.2018.06.004

4. Lisitsyn, A.P., 1994. A Marginal Filter of the Oceans. *Okeanologiya*, 34(5), pp. 735– 747 (in Russian).

5. Fedorov, K.N., 1986. *The Physical Nature and Structure of Oceanic Fronts*. New York: Springer, 333 p.

6. Kaiser, D., Konovalov, S., Schulz-Bull, D.E. and Waniek, J.J., 2017. Organic Matter along Longitudinal and Vertical Gradients in the Black Sea. *Deep Sea Research Part: Oceanographic Research Papers*, 129, pp. 22–31. doi:10.1016/j.dsr.2017.09.006

7. Saraceno, G.F., Pellerin, B.A., Downing, D.D., Boss, E., Bachand, P.A.M. and Bergamaschi, B.A., 2009. High-Frequency in situ Optical Measurements during a Storm Event: Assessing Relationships between Dissolved Organic Matter, Sediment Concentrations, and Hydrologic Processes. *Journal of Geophysical Research. Biogeosciences*, 114(G4), G00F09. doi:10.1029/2009JG000989

8. Ilyin, Yu.P., Repetin, L.N., Belokopytov, V.N. and Goryachkin, Yu., 2012. *Hydrometeorological Conditions of the Ukrainian Seas. Vol. 2.* Sevastopol: ECOSY-Gidrofizika, 421 p. (in Russian).

9. Lomakin, P.D. and Zavyalov, D.D., 2021. Field of Colored Dissolved Organic Matter in the Azov Sea Coastal Waters. *Proceedings of the T.I.Vyazemsky Karadag Scientific Station – Nature Reserve of the Russian Academy of Sciences*, 6(3), pp. 14–21. doi:10.21072/eco.2021.19.02 (in Russian).

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About the authors:

Pavel D. Lomakin, Leading Research Associate, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russian Federation), Dr.Sci. (Geogr.), professor, **ResearcherID: V-7761-2017**, **Scopus Author ID: 6701439810**, **IstinaResearcherID (IRID): 18321047**, *p_lomakin@mail.ru*

Dmitry D. Zavyalov, Junior Research Associate, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russian Federation), *evilfence@ya.ru*

Contribution of the authors:

Pavel D. Lomakin – general task statement, collection of source information, interpretation of the results, article test writing

Dmitry D. Zavyalov – calculations, interpretation of the results, drawing-up of illustrations

All the authors have read and approved the final manuscript.