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Original paper

Organic Matter in Waters of the Russian Sector of the Caspian Sea

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Abstract

The paper aims to analyse the results of long-term studies of dissolved and suspended organic matter content in the waters of the Northern Caspian and Middle Caspian in the Russian sector of the Caspian Sea. The paper analyses the main sources of input of organic matter, its seasonal and inter-annual variability, features of its spatial distribution and causes (allochthonous organic matter flow, production and destruction, water temperature, sea level changes, etc.) determining the spatial and temporal dynamics of organic matter content. The paper is written on the results of production environmental monitoring conducted at the licensed areas of LLC LUKOIL-*Nizhnevolzhskneft* in 2017–2021. The organic matter amount was estimated by organic carbon. The dissolved organic carbon concentration was found to vary from 0.10 to 9.30 mg/dm^3 in the surface water layer and from 0.10 to 9.60 mg/dm^3 in the bottom layer. The maximum enrichment of waters with dissolved organic matter was noted in the northern part of the water area. The concentration of suspended organic carbon in the surface water layer varied within 0.10–23.40 mg/dm^3, whereas in the bottom water layer it ranged within 0.05–19.40 mg/dm^3. The spatial distribution of suspended organic matter was characterized by seasonal shifts of the area with maximum concentrations northwards. The main factors affecting the organic matter content in water were water temperature, suspended matter concentration in water and hydrogen ion concentration. The level of dissolved and suspended organic matter has not changed in the last 20 years of studies. The dependence of dissolved and suspended organic matter concentrations on environment pH indicates the natural origin of the organic matter in the waters of the monitored sea area.

Keywords: Caspian Sea, productivity, organic matter, dissolved organic matter, suspended organic matter, allochthonous organic matter, autochthonous organic matter

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Органическое вещество в водах российского сектора Каспийского моря

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Аннотация

Цель работы заключается в анализе результатов многолетних исследований содержания растворенного и взвешенного органического вещества в водах акватории Северного и Среднего Каспия в российском секторе Каспийского моря. Проанализированы основные источники поступления органического вещества, его сезонные и межгодовые изменения, особенности его пространственного распределения и причины (сток аллохтонного органического вещества, продукционно-деструкционные процессы, температура воды, изменения уровня моря и проч.), определяющие пространственную и временную динамику содержания органического вещества. Работа написана по результатам производственного экологического мониторинга, проведенного на лицензионных участках ООО «ЛУКОЙЛ-Нижневолжскнефть» в 2017–2021 гг. Количество органического вещества оценивали по органическому углероду. Установлено, что концентрация растворенного органического углерода изменялась от 0.10 до 9.30 мг/дм^3 в поверхностном слое воды и от 0.10 до 9.60 мг/дм^3 в придонном. Областью максимального обогащения вод органическим веществом в растворенной форме была северная часть акватории. Концентрация взвешенного органического углерода в поверхностном слое воды изменялась в интервале 0.10–23.40 мг/дм^3, в придонном – в интервале 0.05–19.40 мг/дм^3. Пространственное распределение органического вещества во взвешенной форме характеризовалось сезонным смещением области максимальных концентраций к северу. Основными факторами, влияющими на содержание органического вещества в воде, являются температура воды, а также концентрация взвешенного вещества в воде и водородный показатель. Уровень содержания растворенного и взвешенного органического вещества за последние 20 лет исследований не изменился. Зависимость концентрации растворенного и взвешенного органического вещества от pH среды подтверждает естественную природу органического вещества в водах исследуемой акватории.

Ключевые слова: Каспийское море, продуктивность, органическое вещество, растворенное органическое вещество, взвешенное органическое вещество, аллохтонное органическое вещество, автохтонное органическое вещество

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Introduction

Potential biological productivity of a marine ecosystem is estimated by organic matter (OM) reserves in the water body. Being a product of vital activity of plants and animals, OM determines physical and chemical properties of water and bottom sediments and serves as a source of nutrients [1)].

[1)] Maystrenko, Yu.G., 1965. [*Organic Matter of Water and Bottom Sediment of Ukrainian Rivers and Water Bodies (the Dnieper and Danube Basins)*]. Kiev: Naukova Dumka, 239 p. (in Russian).

Representative indicators of dissolved organic matter (DOM) and suspended organic matter (SOM) are dissolved organic carbon (DOC) and suspended organic carbon (SOC) concentrations, respectively [1].

In the Caspian Sea, the incoming part of the OM balance is formed by allochthonous and autochthonous organic material, with autochthonous OM playing the leading role [2)]. Phytoplankton is the main producer of autochthonous OM [2)-4)]. Allochthonous OM comes mainly with river runoff [2, 3]. Main items of the consumption part of the balance are the OM bottom sedimentation and consumption during mineralisation [2)].

OM is present in the Caspian waters in dissolved and suspended forms [4]. Carbohydrates and lipids are main biochemical components of DOM [5], while lipids and proteins are those of SOM [3]. OM of allochthonous origin is characterised by a high content of the insoluble fraction [2), 3)].

According to literature, in the Russian sector of the Caspian Sea, the maximum DOM and SOM content is registered in the north-western part of the Northern Caspian, in the estuaries of the Terek and Sulak Rivers, as well as in the hydrologic front zone. The OM concentration decreases seaward [5)] [2, 5].

The OM concentration decreases with depth as a result of aerobic destruction [6]. Biochemical processes intensify in the bottom layer due to periodic turbulence of bottom sediments [6)]. In shallow water areas, OM is distributed uniformly throughout the water column due to intensive mixing [5)].

OM is characterised by seasonal changes: in spring, during phytoplankton blooming, the OM content in the photic water layer increases, and in autumn, it decreases due to the development of destruction and sedimentation [7, 8]. Suspended matter (SM) is the predominant form through which OM transitions from water to sediments [7)].

The rate of destruction of organic compounds depends on water temperature, environment pH and aeration conditions [3)]. Increase in water temperature adds to the intensity of mineralisation of organic compounds [9]. Increase in the environment pH indicates more active OM formation under conditions of production intensification, causing a decrease in the partial pressure of carbon dioxide in water, and OM destruction accompanied by an increase in the partial pressure of carbon dioxide

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2) Datsko, V.G., 1957. [Content of Organic Matter in the Caspian Sea Waters and its Approximate Balance]. *Gidrokhimicheskie Materialy*, XXVII, pp. 10–20 (in Russian).

3) Romankevich, E.A., 1977. [*Geochemistry of Organic Matter in the Ocean*]. Moscow: Nauka, 256 p. (in Russian).

4) Bordovskiy, O.K. and Ivanenkov, V.N., eds., 1979. [*Ocean Chemistry. Vol. 1. Chemistry of Ocean Waters*]. Moscow: Nauka, 521 p. (in Russian).

5) Pakhomova, A.S. and Zatuchnaya, B.M., 1966. [*Hydrochemistry of the Caspian Sea*]. Leningrad: Gidrometeoizdat, 342 p. (in Russian).

6) Fedosov, M.V., 1957. [Chemical Basis of Southern Seas Fodder and their Water Regime]. *Informatsionny Sbornik VNIRO*, (1), pp. 14–19 (in Russian).

7) Romankevich, E.A., Artemiev, V.E., Belyaeva, A.N. and Lyutsarev, S.V., 1982. [Biogeochemistry of Dissolved and Suspended Organic Matter in the Ocean]. In: A.V. Sidorenko and A. A. Geodekian, eds., 1982. [*Organic Geochemistry of Waters and Exploration Geochemistry: Proceedings of the 8^{th} International Organic Chemistry Congress*]. Moscow: Nauka, pp. 7–17 (in Russian).

leads to a decrease in pH. Oxygen, as the main oxidant in the bottom water layer, is used for mineralisation of organic compounds. The decrease in oxygen concentration in water depends on the amount of oxidised OM [4)].

An important role in OM mineralisation belongs to bacteria capable of decomposing dead OM (including oil products) and transforming its destruction products into forms suitable for assimilation by aquatic vegetation [8)] [10].

Study of the peculiarities of OM content and distribution in water bodies subject to organic pollution is especially relevant.

In the Russian sector of the Caspian Sea, deterioration of the quality of the marine environment has been observed in the modern period, which is primarily caused by the inflow of pollutants, including organic compounds (petroleum hydrocarbons, phenols, organochlorine pesticides, synthetic surfactants) from the Volga, Terek, and Sulak rivers [9)] [11–15]. In addition, eutrophication has been intensively occurring in the Northern Caspian and Middle Caspian, leading to an increase in the DOM and SOM amount [4, 16].

Sea level fluctuations result in quantitative changes in OM. Recent studies of OM distribution in the Caspian Sea waters in 2010–2015 showed that during that period of sea level decline, the DOC concentration had been almost unchanged [10]. However, the Caspian Sea level has decreased by more than 70 cm since 2016, and its further decline is predicted [17].

Under these conditions (continuing pollution, eutrophication, sea level decrease), it is necessary to estimate the OM content in the Caspian Sea waters in the modern period.

The work aims to determine the main sources of organic matter in the water area of the Russian sector of the Caspian Sea and the factors determining the spatial and temporal dynamics of the content of organic matter, its suspended and dissolved forms.

Materials and methods

The paper is written on the results of production environmental monitoring conducted at the licensed areas of LLC *LUKOIL-Nizhnevolzhskneft* in 2017–2021. Monitoring was carried out twice a year (spring–summer and autumn periods). Samples were taken consecutively at 58 stations (Fig. 1) in the surface and bottom layers.

First day analyses (water temperature, pH) were carried out by standard methods. Water samples (347 items) were processed in accredited laboratories. Nationally recognised test methods, certified measurement procedures, calibrated and verified measuring instruments were used in the chemical analyses. The amount of organic matter was estimated by organic carbon in accordance

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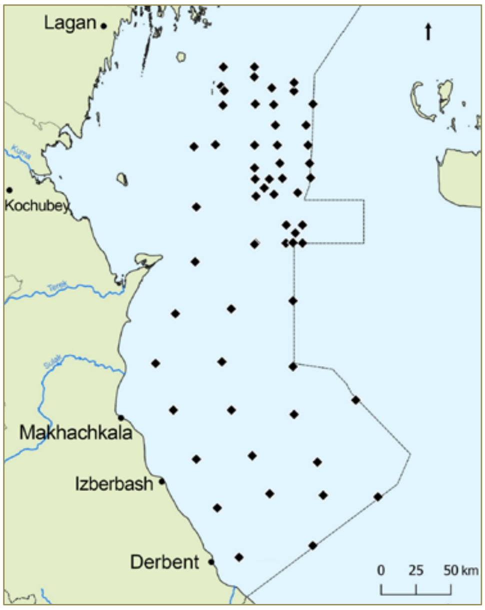
[8)] Bordovsky, O.K., 1964. [*Accumulation and Transformation of Organic Matter in Marine Sediments (Study on the Origin of Oil)*]. Moscow: Nedra, 128 p. (in Russian).

[9)] Gurpanbur, Sh.B., 2010. [Ecological Problems of the Caspian Sea]. *Molodoy Ucheny*, I(5), pp. 128–131 (in Russian).



F i g . 1 . Sampling scheme

with GOST 31958-2012. Statistical analysis was carried out according to paper [10].

Results and discussion

The hydrochemical regime was characterised by an increase in water temperature from spring to summer with preservation of sufficiently high temperature values in autumn (Table 1). Seasonal increase in hydrogen index values indicates production activation in summer and autumn period. The decrease in the amount of suspended sediment in summer and autumn is explained by the seasonal decrease in the volume of solid runoff with the Volga waters.

The DOC concentration varied from 0.10 to 9.30 mg/dm^3 in the surface layer and from 0.10 to 9.60 mg/dm^3 in the bottom layer (Table 2). On average, during the entire study period, the DOC content was higher near the surface due to the OM primary production in the photic layer and OM decomposition in the water column. However, due to the shallowness of the study area, vertical differences were minimal. The correlation between the values of DOC concentration in the surface and bottom layers was revealed. In spring, under high flood conditions and, consequently, high hydrodynamic

T a b l e 1 . Average values of hydrochemical indicators

Season	Water temperature, °C		Water pH		Suspended matter, mg/dm^3	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
Spring	15.5	11.1	8.36	8.37	6.44	5.76
Summer	25.6	19.6	8.40	8.38	6.21	4.91
Autumn	19.5	17.0	8.46	8.43	2.88	2.51

[10] Smagunova, A.N. and Karpukova, O.M., 2012. [*Methods of Mathematical Statistics in Analytic Chemistry*]. Rostov-on-Don, Feniks, 346 p. (in Russian).

T a b l e 2 . Concentration of organic carbon in the water of the Northern Caspian, mg/dm^3

Season	Layer	Dissolved organic carbon		Suspended organic carbon	
		Range	Average	Range	Average
Spring	Surface	0.10–9.30	3.12	0.20–23.40	3.06
	Bottom	0.10–9.60	2.81	0.10–19.40	2.49
Summer	Surface	1.50–4.11	2.35	0.10–13.30	1.64
	Bottom	1.18–3.50	2.19	0.10–9.20	1.36
Autumn	Surface	0.75–6.00	2.43	0.10–6.86	1.17
	Bottom	0.45–5.00	2.21	0.05–4.80	0.96

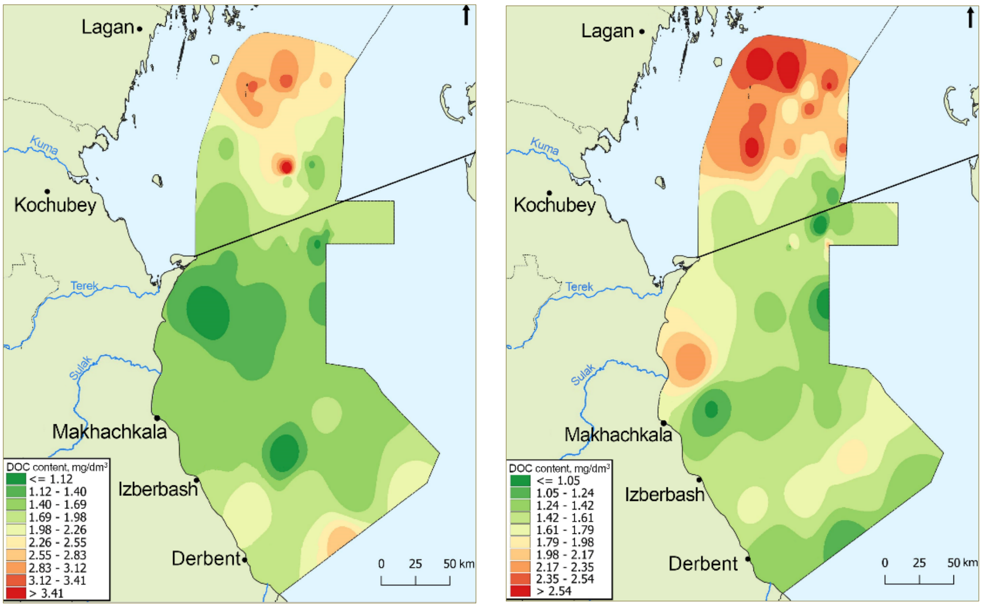
activity, the correlation coefficient (r) was lower (r = 0.48; n = 134; α = 0.05) than in summer (r = 0.74; n = 72; α = 0.05) and autumn (r = 0.79; n = 142; α = 0.05).

Despite the increase in the hydrogen ion concentration (pH) indicating the activation of OM primary production (Table 1), a decrease in the DOC content was observed from spring to autumn, both in the surface and bottom layers, which is explained by the increased insolation inhibiting photosynthesis in the summer and autumn period [11)].

During the study period, the area of maximum DOC concentration was the northern part of the water area (Fig. 2).

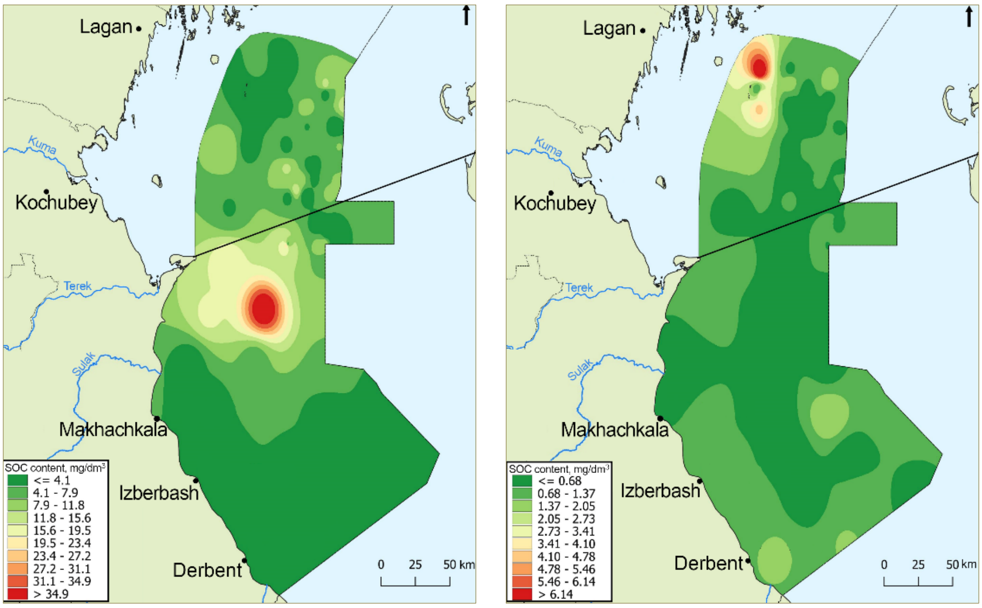
The SOC concentration varied in the range of 0.10–23.40 mg/dm^3 in the surface water layer and in the range of 0.05–19.40 mg/dm^3 in the bottom water layer (Table 2). The SOC vertical distribution and seasonal dynamics repeated changes in the SM concentration (Table 1). The maximum SOC values recorded in the spring period are explained by the input of allochthonous organic matter with the Volga River runoff during the high flood period. However, from spring to autumn, the correlation between SOC content in the surface and bottom water layers became weaker. Thus, correlation coefficient was 0.66 (n = 134; α = 0.05) in spring; 0.61 (n = 72; α = 0.05) in summer; 0.48 (n = 142; α = 0.05) in autumn. The decrease in the correlation ratio between these parameters is due to the fact that in spring SOC was a part of allochthonous (hard-to-mineralise) OM supplied with the Volga waters during high floods, and almost did not decompose in the water column, while in autumn it was a part of autochthonous (easily acidifiable) OM mineralised in the whole water column.

[11)] Boulion, V.V., 1983. [*Primary Prodution of Plankton of Inland Water Bodies*]. Leningrad: Nauka, 150 p. (in Russian).



a ***b***

F i g . 2 . Spatial distribution of dissolved organic carbon (mg/dm^3) in the surface water layer in spring 2020 (*a*) and autumn 2021 (*b*). The line denotes the border between the Northern and Middle Caspian



a ***b***

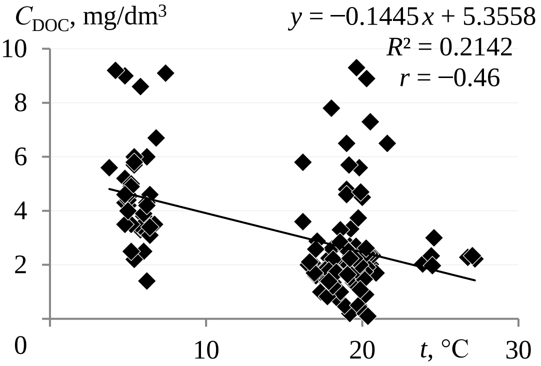
F i g . 3 . Spatial distribution of suspended organic carbon (mg/dm^3) in the surface water layer in spring 2020 (*a*) and autumn 2021 (*b*). For the line notation see Fig. 2

The SOC spatial distribution corresponded to the DOC distribution in autumn (Fig. 3). In the spring period, the area of the highest values was located on the traverse of the Agrakhan Peninsula, which can be caused by the Volga water export to this area against the background of increased water flow.

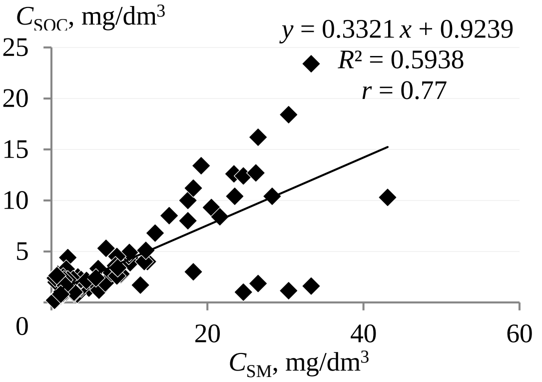
No statistically significant correlation between the content of DOC and SOC was found throughout the study period. The level of content as well as the characteristic features of the spatial distribution of DOC and SOC have not changed over the last 20 years of studies [18].

In the spring period, the DOC concentration was inversely related to water temperature. Correlation coefficient was –0.46 (Fig. 4) for the surface layer and –0.35 for the bottom one (n = 137; α = 0.05). The SOC content was in direct correlation with the SM amount: r = 0.77 (surface) (Fig. 5) and r = 0.71 (bottom) with n = 137; α = 0.05. This indicates that SOC occurs as part of allochthonous, hard-to-mineralise OM in the spring period.

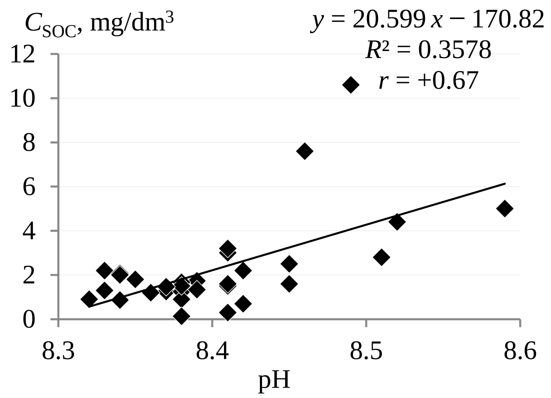
Correlation dependence of DOC and SOC concentration on water pH was revealed in summer. The SOC dependence of pH (r = 0.67 and 0.62 for the surface (Fig. 6) and bottom layer, respectively) was stronger than the DOC dependence of pH (r = 0.48 and 0.57 for the surface and bottom layer, respectively). For all the above mentioned dependencies, n = 74; α = 0.05.



F i g . 4 . Dependence of dissolved organic carbon C (mg/dm^3) on water temperature (°C) in the surface water layer during spring



F i g . 5 . Dependence of suspended organic carbon concentration (mg/dm^3) on suspended matter concentration (mg/dm^3) in the surface water layer during spring



F i g . 6 . Dependence of suspended organic carbon concentration (mg/dm^3) on pH in the surface water layer during summer

No statistically significant correlations were found in the data array for the autumn period.

The seasonal dynamics of SM, DOC and SOC differed at different stages of the marginal filter.

According to literature, the maximum amount of SM is registered in the "mud area" (water area with salinity not exceeding 4‰) [19]. However, our studies revealed that this pattern was observed only in summer and autumn (Table 3). In spring, during high floods, the main part of SM is carried further seaward. The increase in the SM and SOC content was observed in summer, in the DOC content – in spring.

In the "elementorganic area" (water area with salinity of 4–7‰), transition of organic substances into bottom sediments takes place as a result of flocculation and sorption activation [19]. Decrease in DOC concentration in water in the "elementorganic plug" in comparison with the "mud area" is observed only in spring. In summer and autumn, SOC decreases in the "elementorganic plug" (in autumn only in the surface layer).

In the "biological part" of the marginal filter (with salinity over 7‰), the OM bioassimilation takes place due to intensification of living organisms activity. The DOC and SOC concentration decreases compared to the OM content in the "elementorganic area". The DOC concentration decreased insignificantly, the SOC concentration decreased 3.3 times in the surface water layer and 4 times in the bottom water layer in summer. The SOC sharp decrease near the surface is a consequence of destruction, which is more intensive in the surface water layer under conditions of high oxygen saturation of water. Sharp decrease in the SOC amount in the bottom horizon is probably caused by the development of such filter-feeding molluscs as *Cerastoderma glaucum* (Bruguière, 1789) inhabiting at salinities of at least 5‰; *Monodacna colorata* (Eichwald, 1829), optimum salinity for which is 6–10‰; *Didacna protracta* (Eichwald, 1829) preferring salinities above 8‰, etc., in the biological part of the marginal filter [20, 21].

T a b l e 3 . Average concentration of suspended and organic substances in the water of the Northern Caspian, mg/dm^3

Season	Suspended matter		Dissolved organic carbon		Suspended organic carbon	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
Salinity < 4‰						
Spring	1.55	1.60	7.75	5.75	1.25	1.05
Summer	11.15	3.55	2.38	2.32	7.80	6.68
Autumn	7.33	1.42	2.11	2.00	2.42	0.10
Salinity 4–7‰						
Spring	6.40	5.52	3.53	2.93	3.36	2.51
Summer	9.22	9.12	2.82	2.56	4.12	4.07
Autumn	3.83	4.06	3.08	2.54	1.59	1.23
Salinity > 7‰						
Spring	6.53	5.86	2.99	2.75	3.06	2.51
Summer	5.82	4.62	2.32	2.16	1.25	1.01
Autumn	2.71	2.36	2.37	2.17	1.10	0.94

Conclusion

The DOC and SOC concentration in the surface water layer of the Russian sector of the Caspian Sea is higher than in the bottom one due to the primary production of OM in the photic layer and decomposition of OM in the water column. Seasonal dynamics is characterised by a decrease in DOC and SOC from spring to autumn, which is explained by natural hydrochemical reasons (increased insolation inhibiting photosynthesis in the summer and autumn period, beginning of the destruction development in autumn and decrease in allochthonous OM input with the Volga River runoff).

The main factors affecting the OM content in water are water temperature (negative trend) and the amount of suspended sediment and water pH (positive trend).

The level of DOM and SOM has not changed in the last 20 years of studies. The dependence of DOM and SOM concentrations on environment pH assumes the natural origin of the organic matter in the waters of the monitored sea area.

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