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MARINE BIOLOGY

Optical Characteristics and Distribution of Chromophoric Dissolved Organic Matter in Onega Bay (White Sea) during the Summer Season (Findings from an Expedition from June 22 to 26, 2015)

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Abstract—Onega Bay waters are characterized by a high content of chromophoric dissolved organic matter (CDOM). The absorbance spectra and fluorescence intensity (excitation wavelength 455 nm, emission wavelength >680 nm) were used to assess the distribution of CDOM content in water filtered through a GF/F filter. The CDOM content at different points in Onega Bay showed more than a fourfold difference, as inferred from the measured values. The CDOM content in surface waters was, as a rule, higher than in the deeper horizons. A higher CDOM content was measured near the Onega River, near the middle part of the Onega shore, and near the Pomor shore opposite the town of Belomorsk. River runoff is the major source of CDOM in Onega Bay water. The CDOM chemical composition in Onega Bay waters was heterogeneous. The ratio of the fluorescence intensity to the absorbance value was higher near the mouths of rivers and in intensive mixing zones than in water characterized by high salinity. A highly significant linear correlation ($R^2 = 0.7825$) between water salinity and CDOM fluorescence intensity was demonstrated. The contribution of fluorescent compounds to river runoff CDOM is substantially higher than the contribution to the composition marine CDOM.

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INTRODUCTION

Water quality in the coastal parts of seas results from processes in terrestrial and marine ecosystems. Dissolved organic matter derived from both autochthonous and allochthonous sources is among the main carbon pools in coastal water ecosystems [16]. In ocean chemistry, matter not retained by filters with a 0.45–1 μm pore size is regarded as dissolved matter [12].

An inverse correlation between salinity and the concentration of dissolved organic matter is often observed in coastal waters, since rivers are the main source of dissolved organic matter in these areas [17]. The portion of dissolved organic matter capable of light absorption is usually termed chromophoric dissolved organic matter (CDOM). The chemical characteristics that govern these optical properties also determine the high photochemical activity of CDOM [20]. The optical properties of CDOM are often used as characteristics of bay and liman water masses [23]. CDOM is an important parameter for satellite monitoring, because it has a decisive effect on the optical properties of water [2].

The White Sea is a relatively small waterbody that includes several areas with diverse hydrological, hydrochemical, and other parameters [13]. Onega Bay has been much less well studied than other parts of the White Sea. The hydrophysical characteristics of the Onega Bay determine its shallowness and considerable tidal effects. The strong influence of river runoff and horizontal structure of the thermohaline, combined with the vertical homogeneity of water, are characteristic of Onega Bay. Water masses with a dissimilar structure are separated by frontal zones. Transfrontal transitions, largely determined by periodic tidal currents and the effect of winds, cross the fronts [6]. The patchiness and high seasonal and interannual variability of the physicochemical parameters of the water state is characteristic of this waterbody. Changes in climate and the ice situation, combined with anthropogenic load, has led to shifts in the hydrochemical regime and structural and production characteristics of the White Sea [4, 5]. A high CDOM concentration is characteristic of waterbodies of boreal and Arctic regions. Remote probing of these waters is hindered by the high absorbance of CDOM, which determines the very low reflective capacity for visible light (400–700 nm) [9, 22]. Since the CDOM content in Onega Bay is high, assessment of water mass status, including CDOM distribution, by contact methods appears to be a relevant research topic. The aim of the present study was to assess the CDOM distribution in Onega Bay in early summer 2015 using contact optical methods.

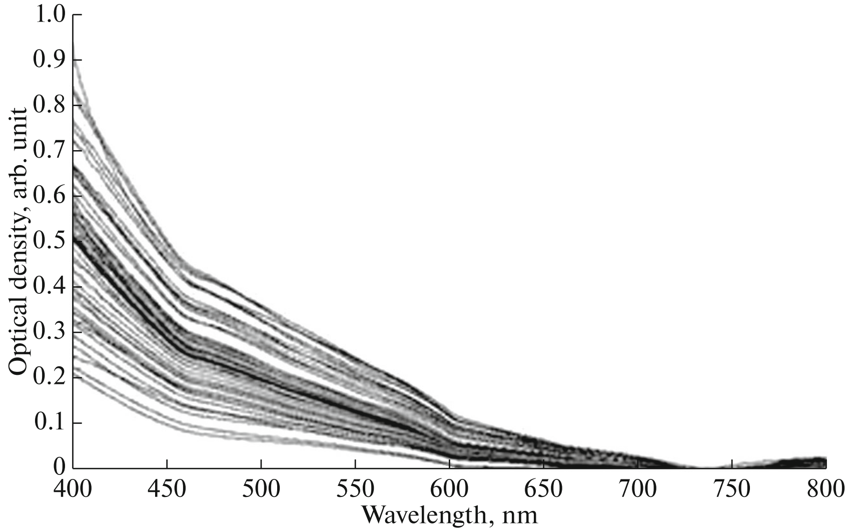

Fig. 1. CDOM absorbance spectra in Onega Bay water (White Sea).

MATERIALS AND METHODS

The distribution and optical characteristics of CDOM in Onega Bay were analyzed from June 22 to 26, 2015, aboard the R/V *Ekolog*. Water samples from a bathometer were passed through a GF/F fiberglass filter (Whatman) with a pore size of approximately 0.7 μm to remove suspended particulate matter.

The absorbance characteristics of CDOM were determined in the integrating sphere cavity [11].

The spectrophotometer for CDOM absorbance measurement was a modification of an Ocean Optics USB 2000 device (United States), which had the following characteristics:

Light source: 100-W halogen lamp, 24 V.

Range 390–800 nm.

Spectral resolution 3 nm.

Baseline drift <0.005 optical density units/h (wavelength 700 nm).

Integrating sphere: 80 mm in diameter with an internal volume of 300 mL.

USB port for data collection and connection to a PC.

The average optical path length in the integrating sphere is approximately 150 cm [11].

The sphere was filled with distilled water to record the baseline for CDOM absorbance spectra registration. A seawater sample filtered through a GF/F filter was placed in the integrating sphere cavity, and the absorbance spectrum obtained was regarded as the CDOM absorbance spectrum.

CDOM fluorescence intensity (F_f) was measured in a 30-mL quartz cuvette of the Mega-25 device [10] with distilled water as the blank. This device was developed for chlorophyll fluorescence measurements and has the following characteristics: LED excitation source with a peak wavelength of 455 nm, peak pulse intensity of 1000 W/m^2, and emission wavelengths >680 nm for fluorescence registration. Measurements of CDOM fluorescence excited by blue light and registered in the chlorophyll luminescence range are of considerable importance for correcting the results of fluorimetric phytoplankton chlorophyll assays in water samples.

RESULTS

The CDOM content in Onega Bay water is high. The typical absorbance spectra for CDOM are shown in Fig. 1. They are close to the regular patterns reported earlier, such as exponential changes in the absorption coefficient with changing wavelength [18]. Absorbance spectra analysis revealed a more than fourfold differences in CDOM content at different points in Onega Bay (Table 1). The CDOM content in near-surface water was, as a rule, higher than in the deeper horizons. The CDOM content at some stations (1_24; 2_25; 3_26; 4_26; 5_26; 1_27) was virtually the same at different depths (Table 1). Considerable CDOM stratification with depth was observed at stations 1_23; 2_23; 4_24; 5_23. Figure 2a shows the CDOM content distribution in the near-surface water of the study area, as inferred from absorbance at a wavelength of 400 nm. The highest CDOM content was detected near the Onega River, near the middle part of the Onega shore, and near the Pomor shore opposite the town of Belomorsk.

CDOMs are known to fluoresce in a broad spectral range [3, 7]. Filtered water irradiated with 455 nm light to excitate fluorescence showed considerable fluorescence intensity at wavelengths >680 nm; the fluorescence was comparable to phytoplankton chlorophyll fluorescence (Table 1). Figure 2b shows the

Table 1. CDOM optical density values at wavelength of 400 nm (arb. units), fluorescence CDOM intensity (F_f, arb. units), and water salinity (SAL, ‰)

Station	Horizon	DOM (400)	F_f	SAL
1_22	0	0.609	210	25.4575
	2	0.677	210	25.4226
	5	0.509	210	25.4447
1_23	0	0.77	390	23.1405
	2	0.671	370	23.7348
	5	0.471	290	24.7233
2_23	0	0.749	430	21.3046
	2	0.725	430	21.3192
	5	0.377	290	25.5133
	10		220	25.4939
3_23	0	0.271	230	25.3078
	2	0.211	225	25.3046
4_23	0	0.327	300	24.3437
	2		285	24.3972
	5	0.294	260	24.9152
	10	0.223	200	25.4874
5_23	0	0.829	300	23.9353
	2	0.724	300	23.9332
	5	0.627	270	24.6201
	10	0.528	240	25.3782
1_24	0	0.4	180	25.9322
	2	0.383	180	25.9322
	5	0.361	180	25.9166
	10	0.348	200	25.9038
2_24	0	0.386	200	25.4002
	2	0.381	200	25.4002
	8	0.348	210	25.4331
	15	0.333	210	25.538
3_24	0	0.842	270	24.2449
	2	0.67	270	24.2468
	4	0.662	255	24.2468
	10	0.576	220	25.2029
4_24	0	0.934	300	23.1469
	2	0.664	280	23.1469
	5	0.596	250	24.2154
	10	0.33	200	25.54
5_24	0	0.465	280	23.8034
	2	0.463	280	23.8034
	5	0.43	280	24.2749
	10	0.245	230	25.2997
1_25	0		150	27.5964
	2		150	27.5964
	4		150	27.5978
	7		150	27.5992
2_25	0	0.562	190	26.7834
	2	0.554	170	26.7809
	5	0.545	170	26.7998
	10	0.53	180	26.8937
	20	0.489	170	27.3341
3_25	0	0.547	160	26.2905
	2	0.533	170	26.2939
	4	0.525	180	26.4655
	10	0.505	180	26.5958
1_26	0	0.828	230	23.40673
	2	0.653	230	23.41564
	5	0.542	240	25.34617
2_26	0	0.442	160	25.83724
	2	0.412	150	25.84683
	5	0.323	160	25.94328
	10	0.378	160	26.20146
3_26	0	0.353	160	26.65978
	2	0.358	150	26.65619
	5	0.347	150	26.81612
	10		210	27.09191
	15	0.321	160	27.08684
4_25	0	0.589	150	26.46233
	2	0.584	160	26.46620
	5	0.562	150	26.47770
	15	0.539	160	26.60213
	20	0.522	150	26.68053
5_26	0	0.568	150	26.12293
	2	0.529	180	26.13538
	5	0.514	150	26.15739
	10	0.508	150	26.16847
	20		140	26.20490
1_27	0	0.567	160	25.86775
	2	0.589	160	25.82948
	5	0.579	150	
	10	0.578	150	
	20	0.563	150	25.87374

(a)

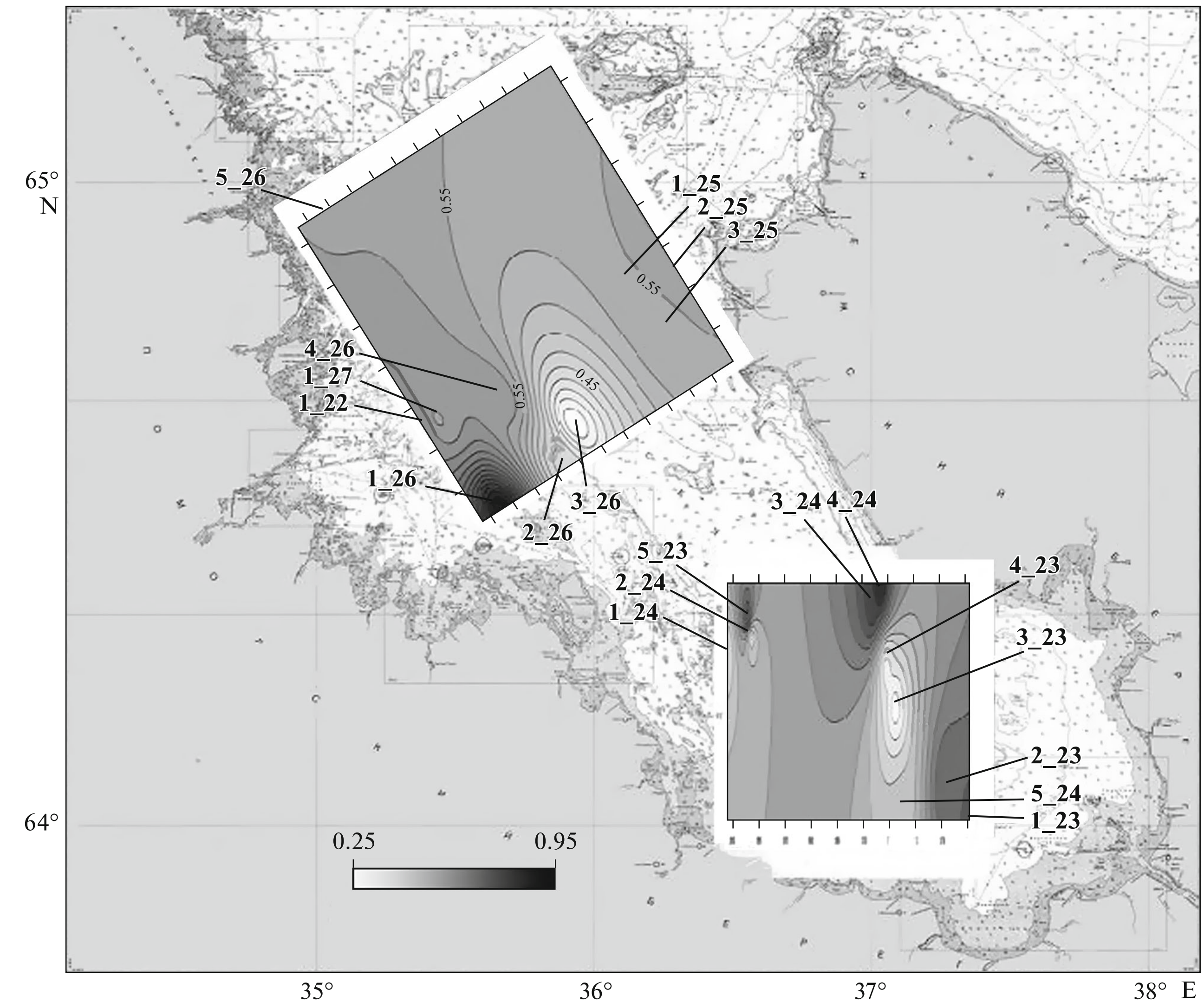

Fig. 2. Maps of CDOM content distribution in surface layer of Onega Bay, White Sea. (a) As inferred from absorbance at wavelength of 400 nm; (b) as inferred from fluorescence intensity at wavelength >680 nm (excitation wavelength 455 nm).

CDOM fluorescence intensity distribution in the near-surface waters of the study area.

DISCUSSION

The CDOM of seawater is a complex mixture of diverse compounds [19]. The CDOM absorbance parameter is an extremely important optical characteristic that determines light absorption by seawater and characterizes the content of chromophoric organic compounds. The value of this parameter makes a significant contribution to the value of diffuse attenuation of underwater irradiance, which characterizes the penetration of solar radiation into the water layer. The CDOM effect in the short-wavelength spectral range is the strongest [2]. A high CDOM content imposes significant limitations on photosynthesis by phytoplankton in some cases [22]. These limitations are often encountered in boreal and Arctic regions.

A correlation between the dissolved organic matter content and the absorbance coefficient at a wavelength of 390 nm was reported in [15]. The typical CDOM absorbance spectrum in the 300–750 nm range is close to an exponential function of the wavelength. Distinct inflections at 450–460 and 600–610 nm and a minimum at 730–740 nm were detected in the absorbance spectra measured in the integrating sphere cavity. The reasons for the elevated optical density of CDOM in the 460–600 nm range remain unclear and require additional studies. This effect may be due to a significant contribution of phycobilins (decay products of cyanobacteria and red algae) to CDOM, because phycobilins are characterized by considerable absorbance in this spectral range [8]. Phytoplankton

(b)

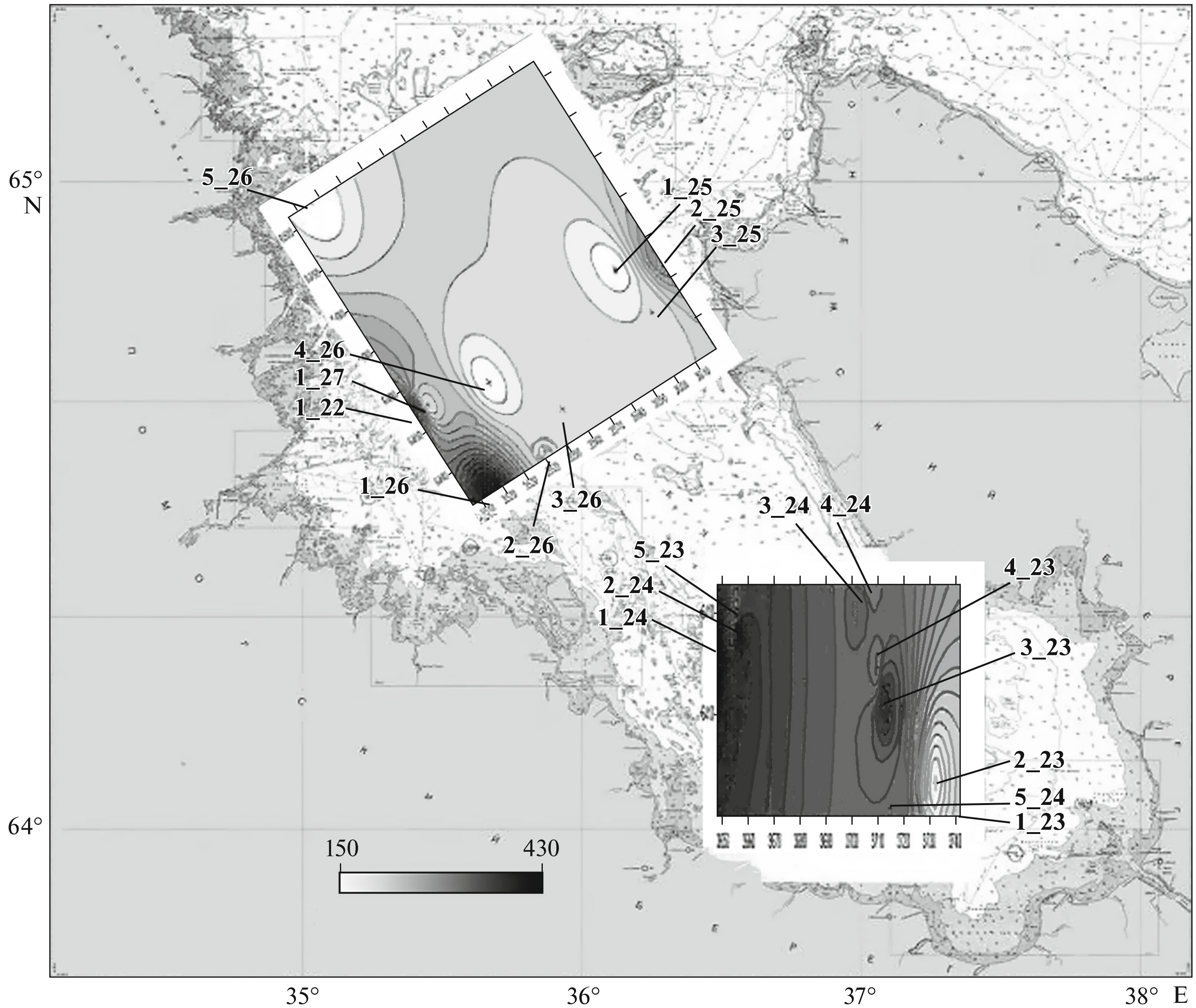

Fig. 2. (Contd.)

analysis showed that these organisms were abundant in the same samples of Onega Bay water [1]. The minimum in the 730–740 nm range of the absorbance spectrum corresponds to fluorescence of phaeopigments, which are products of phytoplankton chlorophyll decay.

Intensive water mixing apparently occurred at some stations (1 24; 2 25; 3 26; 4 26; 5 26; 1 27), where the CDOM content was virtually similar at different depths. Considerable CDOM stratification with depth was observed at stations 1 23; 2 23; 4 24; 5 23, probably due to the presence of water lenses of lower salinity and density (apparently derived from river water) (Table 1).

Different spectral ranges were used as the reference wavelengths for CDOM absorbance [16, 18]. A wavelength of 443 nm was selected as the reference wavelength in [16]. We estimated the CDOM content using absorbance at a wavelength of 400 nm. As shown in Fig. 2a, the highest CDOM content was detected near the Onega River, near the middle part of the Onega shore, and near the Pomor shore opposite the town of Belomorsk. This CDOM distribution indicates river runoff as the major source of these compounds in Onega Bay water.

CDOM-containing waters fluoresce in the range >680 nm upon excitation by blue light. The fluorescence intensity for the 680–750 nm band (Mega-25) was comparable to the fluorescence intensity of phytoplankton chlorophyll (Table 1). The CDOM fluorescence measured under these conditions is due to the presence of phaeopigments, which are the products of photosynthetic pigment decay. No correlation between CDOM content values inferred from the absorbance

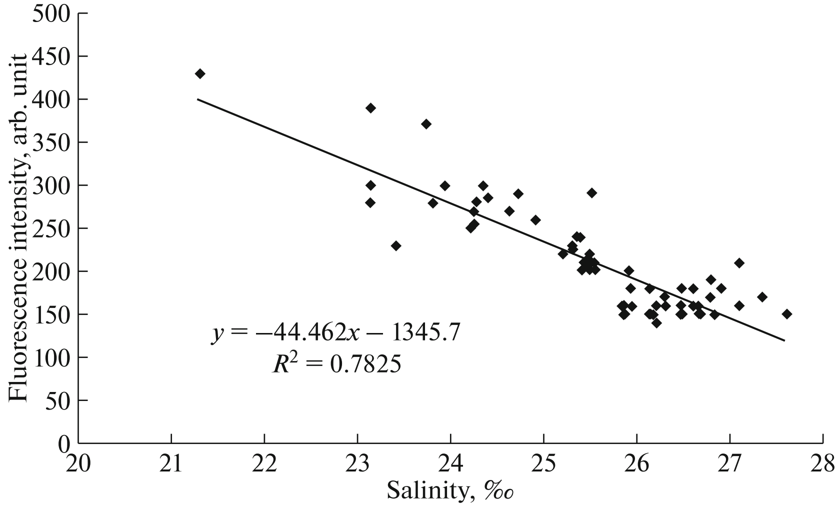

Fig. 3. Ratio of fluorescence intensity at wavelength >680 nm to water salinity for Onega Bay, White Sea.

spectra and fluorescence intensity was detected (the correlation coefficient for these parameters is R^2 = 0.16). This is apparently due to the considerable inhomogeneity in the chemical composition of CDOM in the territory of Onega Bay. The ratio of fluorescence intensity to absorbance was significantly higher for the samples collected near the mouths of rivers and in zones characterized by active mixing than for water samples with high salinity. A highly significant linear correlation ($R^2 = 0.7825$; Fig. 3) between water salinity and the CDOM fluorescence intensity was demonstrated. Thus, the contribution of fluorescent compounds to river runoff CDOM is substantially higher than to the composition of marine CDOM. Similar data were obtained earlier for various coastal water areas [21].

The dependence of the dissolved organic matter concentration on salinity in the marginal filter for the Kem River is $y = -0.1546x + 8.198$; $R^2 = 0.8432$ [14].

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