Nature of organic matter dissolved in seawaters

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The ratio between the dispersal of living phytoplankton and the dissolved organic matter (DOM) in the Black Sea waters was investigated by use of a fluorimetric method. The possibility that DOM appears in sea medium as a result of extracellular excretion due to phytoplankton vital functions was studied. However, data obtained during the tests make us to consider an alternative mechanism of DOM appearance in the sea medium.

A binding role of organic matter in aquatic communities and active participation of its easily assimilable components in inter-organism exchange make it the source of diverse information on the state of an aquatic ecosystem. On the other hand, a characteristic vertical distribution of the fluorescing dissolved organic matter (DOM) makes it indispensable in solving many applied problems, especially in the studies of propagation of deep internal waves, and also in detection of hydrodynamic perturbations and turbulence. However, today, no clear understanding of the nature of DOM and of the mechanism of its appearance in the marine environment has been achieved.

There is a supposition that DOM is excreted in seas and oceans with extracellular waste of plants and animals. As carbon dioxide is fixed in organisms due to photosynthesis, the 5 to 30% fraction of the products of extracellular metabolism are released as soluble organic carbon. Populations of phytoplankton as a whole and its separate species can excrete in the course of their vital activity from 15 to 30% of dissolved organic matter.[1,2] The resulting extracellular products of metabolism include polysaccharides, polypeptides, amino acids, hydroxiacetic acid, and some biologically active compounds.

As was reported in Ref. 3, at the stage of insignificant development of phytoplankton, seawater mostly contains free amino acids. Bada and Lee[4] insist that free amino acids of extremely low concentrations are present only in the surface ocean waters. The presence of these amino acids in seawater is very short-term due to their easy assimilation: they are utilized by sea organisms, react with other organic substances forming polymeric complexes, and are adsorbed by suspended particles. With the increase in phytoplankton excretions, concentration of bound amino acids in seawater grows, which can exist in the form of compounds reminding very small particles of biological detritus. The content of free amino acids in seawater also increases, but then, the quantity of phytoplankton products continues to grow, while the concentration of free amino acids decreases abruptly, and it is bound amino acids that are released into water, which is caused by transformation of organic substance in the cells of phytoplankton. In other words, the concentrations of free and bound amino acids dissolved in seawater are variable characteristics, and like other hydrochemical and biological characteristics, they undergo seasonal variations. We have examined changes in the fluorescence excitation spectra of DOM in the sea surface layers throughout a year.[5] These changes are obviously connected with episodes of seasonal biological productivity of phytoplankton.

This paper is a more detailed study of the mechanism of DOM appearance in aquatic medium and testing whether this process is influenced by the waste products of phytoplankton. The research we have performed consists in the study, by the fluorimetric method, of the related distributions of the living phytoplankton and DOM in waters of the Black Sea. The fluorimetric method is one of the most sensitive methods of analysis. It does not distort the investigated field, and allows us to study the natural seawater without any its preparation, and provides an immediate response of the medium to an action.

Fluorescence of phytoplankton is conditioned by the presence of chlorophyll, which is contained only in its living cells. The chlorophyll fluorescence band is located in the red spectral region with the maximum at ~ 675 nm and the half-width at half maximum of 20 nm. Dissolved organic matter is characterized by a wideband fluorescence located in the blue spectral region. Their fluorescence spectra do not overlap, which makes it possible to use the fluorimeter to detect separately the presence in seawater of the living cells of phytoplankton and DOM. There is no concentration quenching of either phytoplankton-generated chlorophyll fluorescence or that of DOM in seawater. Hence, chlorophyll fluorescence intensity is proportional to the concentration of living phytoplankton cells, and DOM fluorescence intensity is, in its turn, proportional to the concentration of DOM in seawater. Thus, the measured profiles of the fluorescence intensity of chlorophyll and DOM directly correspond to the concentration profiles of the living phytoplankton and DOM, respectively, which allows us to use fluorimetry to study the distribution of phytoplankton and DOM in the waters of seas and

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oceans, as well to trace the dynamics of their concentration changes throughout a year or several years.

Measurement technique and instrumentation

We have carried out our measurements in November, 1990, near the Crimea in the area confined between 43°50′ – 44°15′N latitude and 33°50′ – 34°50′E longitude. Anthropogenic pollution of the sea was excluded here. Measurements were taken every four hours. The closest distance to the shore was 9 miles and the farthest one was 60 miles. The distance between the stations along latitude was 20 miles, and along longitude it was 12 miles.

The profiles of chlorophyll fluorescence intensity and determination of the depths of occurrence of the living phytoplankton cells were measured *in situ* in real time using a Variosens submergible fluorimeter equipped with a gage head with sensors for temperature and pressure.

The fluorescence intensity of DOM was measured in samples of sea water taken from different sea layers, immediately after extraction of the samples. Measurements were performed with a fluorimetric attachment developed to complete the SF-26 spectrophotometer.[6] The fluorescence of DOM was excited by the nitrogen laser ILGI-503 (λ_{gen} = = 337.1 nm), which was installed directly on the spectrophotometer to avoid misalignment of the excitation optical arrangement in case of ship motions. Quantitatively the fluorescence intensity of DOM was evaluated by the rapid test method using the technique of internal ranging described in Ref. 7.

The samples were taken from depths of 0 to 125 m using a bunch of nine BM-48 bathometers. Simultaneously, the reversing thermometers (of TG type) determined water temperature at each of the layers from which the samples were taken. Water salinity in each sample was measured with an onboard electric salinity meter GM-65. Then, using the hydrology data and the standard technique, we calculated the profile of sea water density and other parameters on a personal computer.

Experimental results

The results that we have obtained in the Crimea totally agree with the results of many-year measurements performed in the eastern part of the Black Sea.

Now we can make a general statement that the vertical depth distribution of phytoplankton in the Black Sea has a seasonal character. It is mainly a distribution with a maximum on the surface and a quasi-bimodal distribution with the first maximum in the upper mixed layer and the second one under or within the layer of an abrupt water density change. On the average, maximum depth of occurrence of the living phytoplankton cells does not exceed 60 m, and the width of its layer varies from 20 to 50 m. The seasonal variations of the chlorophyll fluorescence intensity relative to the annual mean intensity are ± 14%.

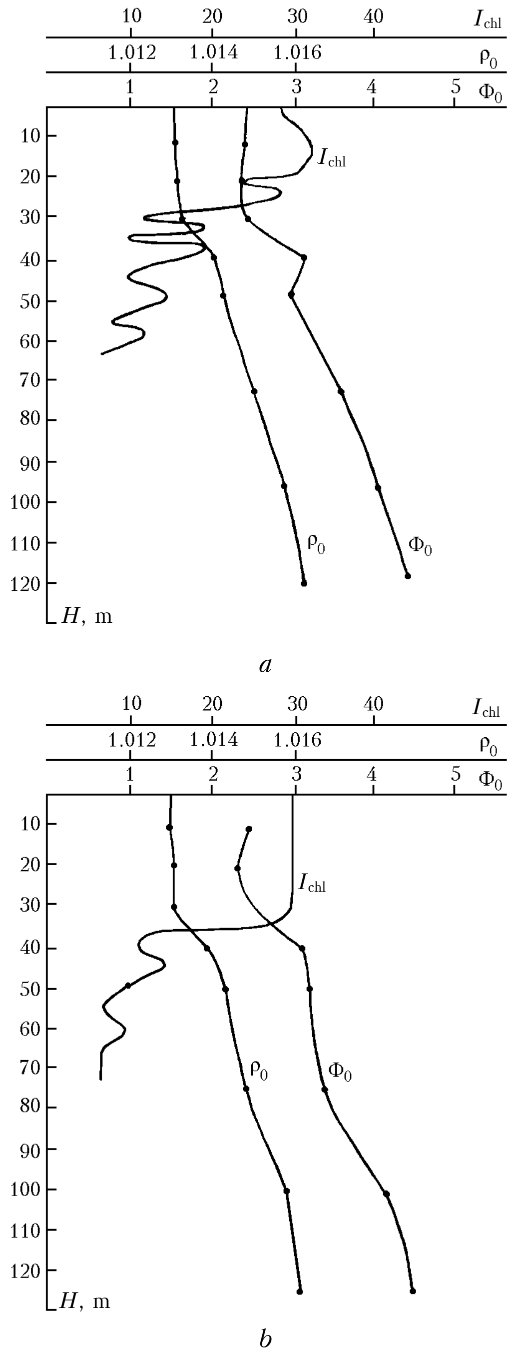

Fig. 1. Profiles of considered characteristics: I_{chl} is the chlorophyll fluorescence intensity expressed in relative units; ρ_0 is the relative seawater density; Φ_0 is expressed in the normalization units of the DOM fluorescence intensity at maximum (L) to the peak intensity of the Raman scattering by water, i.e., L/R.

Vertical distribution of the DOM fluorescence intensity is similar to the seawater density distribution (Fig. 1). If taking into account that the DOM density is close to seawater density (Ref. 8), then this regularity is apparently due to conservative character of the distribution of the fluorescing DOM in seawater, which is determined mainly by the static equilibrium and the internal dynamics of seawaters.

In vertical profiles of the fluorescence intensity of the phytoplankton-generated chlorophyll during the time period studied, the distribution is as follows: the bulk of the phytoplankton is located in the near-surface layer, which is characteristic of this season. Figure 1 illustrates the chlorophyll fluorescence intensity profiles obtained at the boundary longitudes of our test site, wherefrom we see that vertical phytoplankton distribution in the western part of the test site is more structured (Fig. 1*a*) and in the eastern part it is a uniform bulk layer, with the depth reaching 40 m (Fig. 1*b*).

Horizontal distributions of the fluorescence intensity of chlorophyll and DOM in the test site are inhomogeneous and change in their amounts, what shows that the distribution of phytoplankton and DOM in the aquatic medium is “patchy”.

Figure 2 shows the isolines of the chlorophyll and DOM fluorescence intensities at various depths.

The observed differences in vertical profiles and “patches” on horizontal cross sections must result from the internal dynamics of seawaters conditioned among other factors by the set or seasonal sea currents.

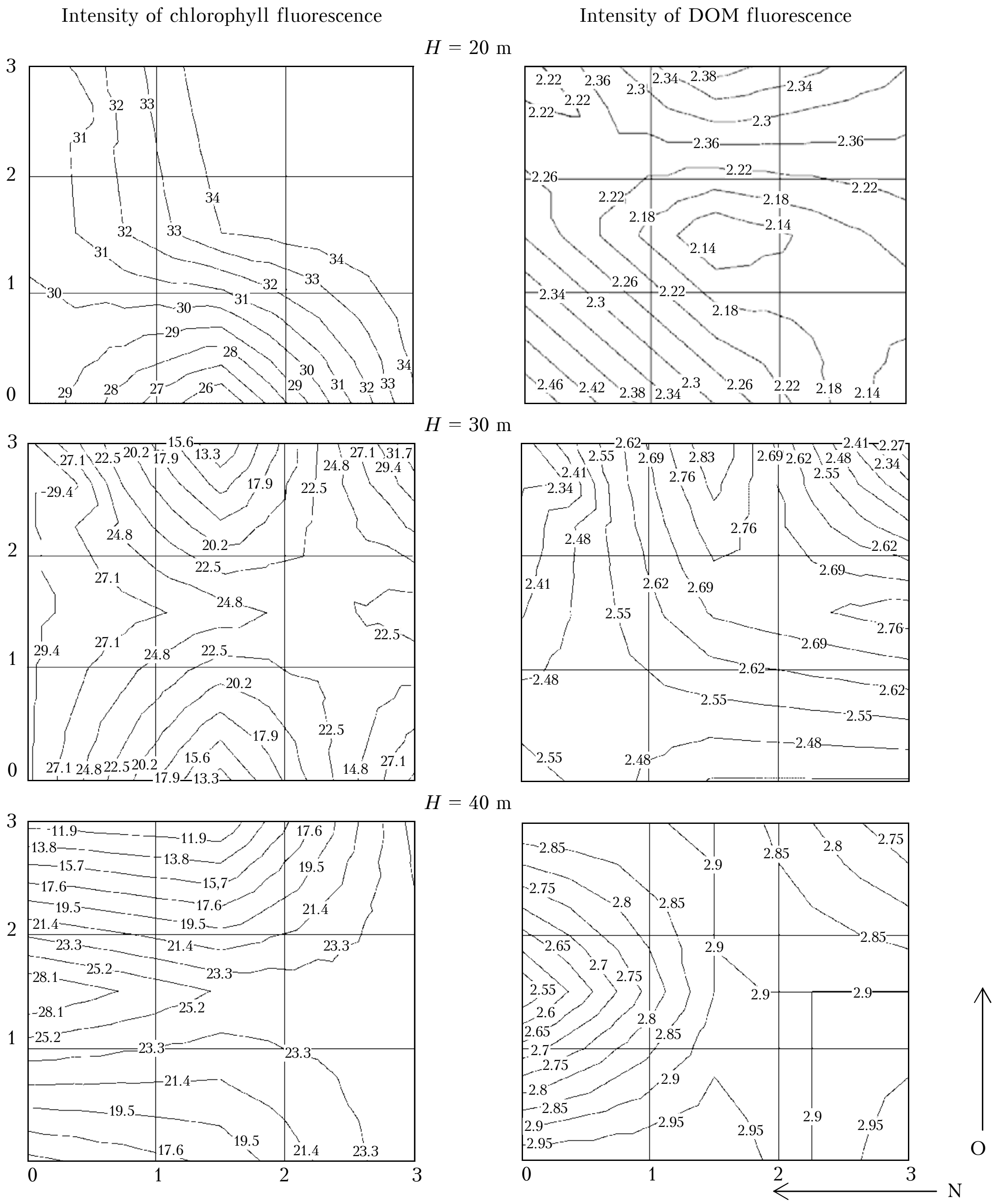

Fig. 2. Isolines of chlorophyll and DOM fluorescence intensities (in relative units) at various depths of the test site.

Comparative distribution of the relative concentration of the living cells of phytoplankton and DOM over horizontal cross sections of the test-site area can be estimated by the chlorophyll and DOM fluorescence intensity distributions shown in Fig. 3.

Discussion of the results

As noted above, DOM density is close to that of sea water. According to the Stokes equation, its vertical movement in this case is possible only with the movement of water or, if adsorbed, on the sedimenting suspended organics. Thus, we find disputable the assumption that DOM appears in sea water as an extracellular phytoplankton waste in the photic zone, and then with gravitational sedimentation it distributes over the whole water column. If it were true, DOM would get accumulated in the areas where the living phytoplankton is present and we would observe here distinct maxima of DOM fluorescence. But the analysis of the vertical profiles of the fluorescence intensity of chlorophyll and DOM shows that the region of the highest concentration of the living phytoplankton cells is characterized by the lowest fluorescence intensity of DOM (see Fig. 1). Also, according to long-term observations, such interrelation of these parameters in the Black Sea is kept both during the period of intensive phytoplankton bloom and after it.

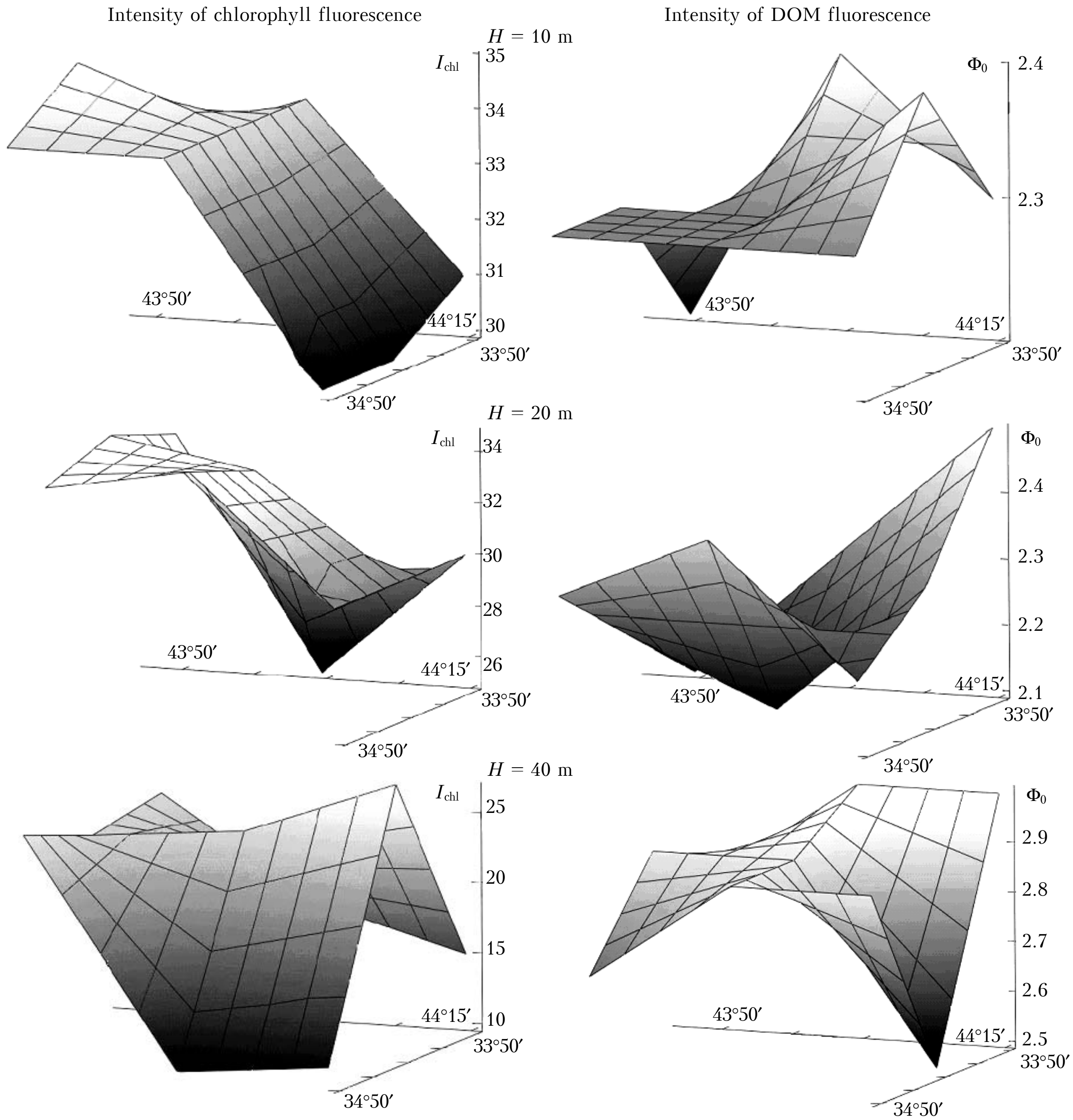

Fig. 3. Horizontal cross sections of the fluorescence intensity of chlorophyll and DOM over the test site.

The interrelations of the fluorescence intensity of chlorophyll and DOM over the horizontal cross sections have the same character. The measurements we have performed in the test site (see Fig. 3) and long-term measurements in the eastern part of the Black Sea show that the fluorescence intensity distributions of chlorophyll and DOM are mutually quite opposite. In other words, the regions with highest concentrations of the living phytoplankton cells correspond to the regions with the lowest DOM concentrations and *vice versa*.

Thus, the study of interrelations of the fluorescence intensity profiles of chlorophyll and DOM in the Black Sea waters helped us to elucidate that in the zone of most intense phytoplankton productivity, where due to this vital activity the concentration of its metabolism products and extracellular waste is the highest, the content of fluorescing DOM is minimum. At the same time, in the deeper sea layers, where there are no living phytoplankton cells, the concentration of DOM significantly exceeds its level in the photic zone and continues to grow (see Fig. 1). Hence, we may conclude that the extracellular waste of phytoplankton is not the main source of DOM in the marine environment, thus proving the supposition (Ref. 9) that water-soluble organic matter appears in the sea in a different way. This follows from the theoretical calculations presented in Ref. 10.

Most likely, this substance forms inside the particles of suspended organics, where the conditions for its formation are most favorable. Transportation of the soluble organic substance to marine environment occurs with its diffusion and outwash from the dying and decomposing suspended organics during sedimentation of the latter.

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