Relation between the parameters of laser-induced fluorescence of seawaters and the seawater type

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The fluorescence spectra of seawaters of different types were studied in some regions of the Pacific Ocean. It is shown that different bio-optical types of the seawaters can be separated based on the type of correlation between the integral characteristics of spectra of the laser-induced fluorescence of chlorophyll A and the organic matter dissolved in seawater.

Knowledge of the origin of organic matter in seawaters is very important for solving some problems as, for example, the determination of the class of seawater. Seawater is usually classified into the first and second class in accordance with the origin of organic matter dissolved and suspended in it. If the main source of organic matter is phytoplankton, then water is classified as the first type; otherwise, we deal with the second type of seawater.[1–3] However, this classification is conditional, because it can be done precisely only in the limiting cases. Thus, open waters of the ocean and shelf waters far from sources of terrigenic organic matter belong to the first class. Waters of the second class are, as a rule, shelf waters situated near local sources of organic matter. However, a great number of situations can occur, in which the amount of dissolved organic matter coming from sources of different types is of approximately same value.

The information on the type of seawater is also important for correct interpretation of the data of remote sensing of sea color when measuring the chlorophyll A concentration. Thus, when using the algorithms of the green/blue ratio, almost same values of regression coefficients can be used for waters of the first type in different regions of the World Ocean.[1] At the same time, for seawaters of the second type the error in reconstruction of the chlorophyll A concentration from the spectra of upward going radiation increases significantly if the same regression coefficients are used for different regions.[4,5] So, the corresponding sub-satellite measurements should be conducted in the regions under study.

The technique of laser excitation of seawater fluorescence has been widely used in recent years to determine the chlorophyll A concentration (see, e.g., Refs. 6 and 7). This technique also allows separating the contributions of the fluorescence signals from the dissolved organic matter (DOM) and living phytoplankton (using the chlorophyll A fluorescence line) to the total signal of fluorescence excited by laser radiation in seawater.

Figure 1 shows an example of the seawater fluorescence spectrum induced by laser radiation at 532 nm. The spectrum was recorded in a region of the Pacific Ocean in spring season. It can be divided into three independent components: Raman spectrum of water (wavelength from 635 to 660 nm in the case of excitation by laser radiation at 532 nm), chlorophyll A fluorescence line at 680 nm, and the broadband spectrum that makes up the background for the former two bands. The broadband spectrum ranges practically from the wavelength of sounding radiation and slowly falls off to the red region. Using the least squares method, we can represent the actual spectrum as a sum of three components (with the relative error of approximation about several percent), as is shown in Fig. 1. In this case, the Raman spectrum is presented as a sum of two Gaussian curves with the fixed half-widths and positions.[8] The fluorescence spectrum of the DOM is described by a function similar to the Weibull distribution with four parameters.[9] The chlorophyll fluorescence line was described by a Gaussian curve.

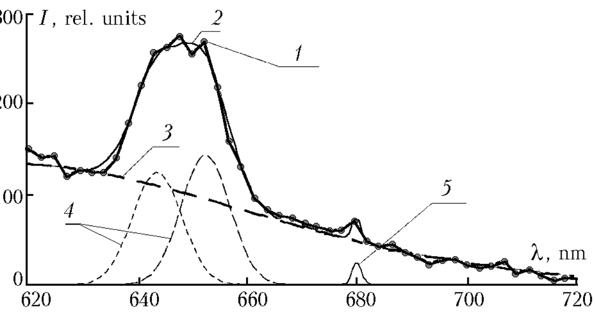

Fig. 1. Resolution of the fluorescence spectrum of seawater: experiment (*1*); regression curve (*2*) and its spectral components: DOM (*3*), Gaussian curves of the Raman spectrum (*4*), chlorophyll A (*5*).

The nature of the fluorescence spectra of chlorophyll A and the Raman spectrum is quite clear. At the same time, the structure of the broadband fluorescence spectrum of the dissolved organic matter is very complicated, and regularities of formation of its spectral composition depending on the composition of the organic matter dissolved in seawater, especially, for seawaters of the second class or polluted waters are practically not understood.

In this paper, we undertake an attempt to find the relations between the spectral parameters of the chlorophyll A fluorescence and the integral characteristics of the broadband part of the DOM fluorescence spectrum in some waters of the Pacific Ocean. Toward this end, the spectra of seawater fluorescence induced by the second harmonic of a Nd:YAG laser with the wavelength of 532 nm were recorded. The measurements were conducted from aboard a moving vessel; the experimental setup is described in Ref. 5. The design of the flow-through laser fluorimeter we used allowed the seawater temperature and salinity to be measured along with the chlorophyll A concentration in the same portion of seawater. The experiments were conducted in the southern and central parts of the Pacific Ocean, in the Sea of Japan and Sea of Okhotsk during the mission of the *Akademik Lavrentiev* research vessel in 1993 and in the mission of the *Nadezhda* sailing vessel in 1997–1998. The sections of the routes where we conducted the measurements are shown in Fig. 2.

For analysis of the results, we selected the measurements conducted at the sections, where the type of seawater could be determined *a priori* (for example, open areas of ocean waters or shelf waters). To determine the correlation between the dissolved organic matter and chlorophyll A in the studied water areas, we have found the dependence of the area under the chlorophyll A fluorescence band S_{chl} (curve *5* in Fig. 1) on the area bounded by the broadband DOM fluorescence spectrum S_{DOM} (curve *3* in Fig. 1) after the corresponding resolution of the spectra as shown in Fig. 1. Figure 3*a* generalizes the measured results obtained along the four sections of the route shown in Fig. 2*b* (voyage of the *Nadezhda* sailing vessel in 1998). The values of the integrals of the broadband DOM fluorescence spectrum and the chlorophyll A fluorescence spectrum in relative units are plotted as axes. Figure 3*b* shows the same results separately for each region.

The figures demonstrate marked clusterization of the points presenting the measured results. Practically all the data correspond to open oceanic waters. They all, except for the region 4 (February 11–12, 1998, Tasmanian Sea), demonstrate a good correlation between S_{chl} and S_{DOM}. The relative rms deviations from the straight lines of the regression for the regions 1 and 2 are 0.08 and 0.1, respectively. Such a narrow scatter of the measured data is indicative of a strong correlation between the phytoplankton and the dissolved organic matter in these regions. Moreover, the tangent angles of the regression straight lines are very close in these regions. In the region 3, the scatter of values about the regression straight line is 1.5 times wider than in the first two regions. Nevertheless, points are apparently grouped about the regression line. This indicates that in the region 3 the integral parameters of the fluorescence spectra of the DOM and chlorophyll A correlate rather well. Consequently, the main contribution to formation of the dissolved organic matter in these regions comes from plankton, i.e., water of the regions 1–3 can be considered as the seawater of the first class.

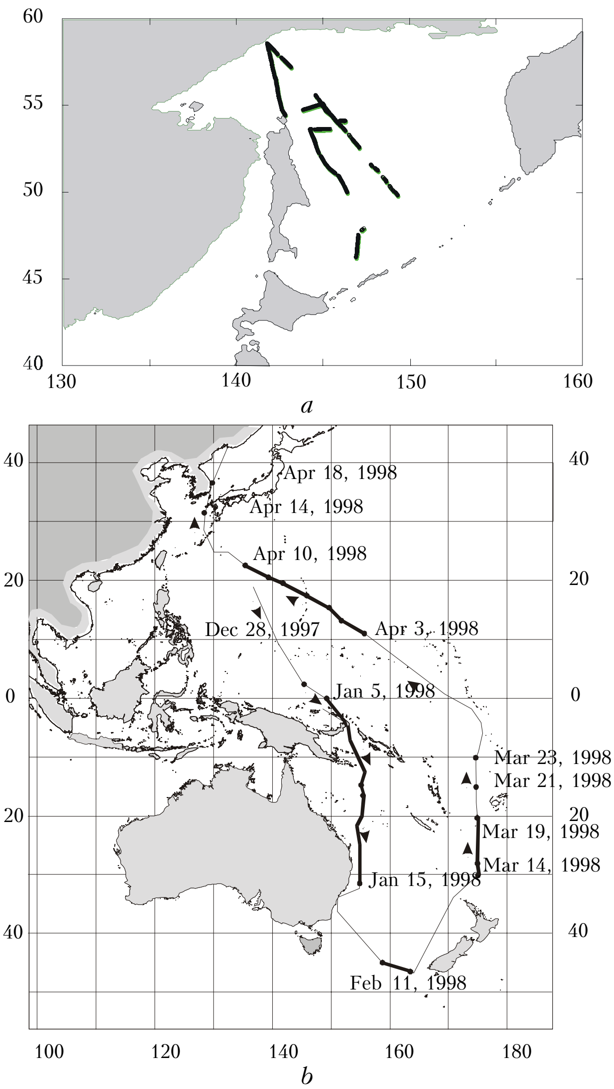

Fig. 2. Routes: Sea of Okhotsk, 1993 (*a*), Pacific Ocean, 1997–1998 (*b*).

Another situation is observed in the region 4, in the Tasmanian Sea. One can see two groups of data with different mean values of the chlorophyll A concentration. There is almost no correlation between the studied parameters in both clusters, because the scatter of points about the centroids of the clusters is rather wide. This allows us to suppose that there is an additional source of the DOM in this region. Actually, in February, waters of the East Australian Stream surrounding the Australian shelf and waters of the Westerly Current (circumpolar) mix in the region 4 (Ref. 10). The waters of the Westerly Current are rich in the dissolved organic matter, which serves as an additional source of DOM in this region. From the viewpoint of determination of the type of seawater, the waters of the region 4 fall into the second class.

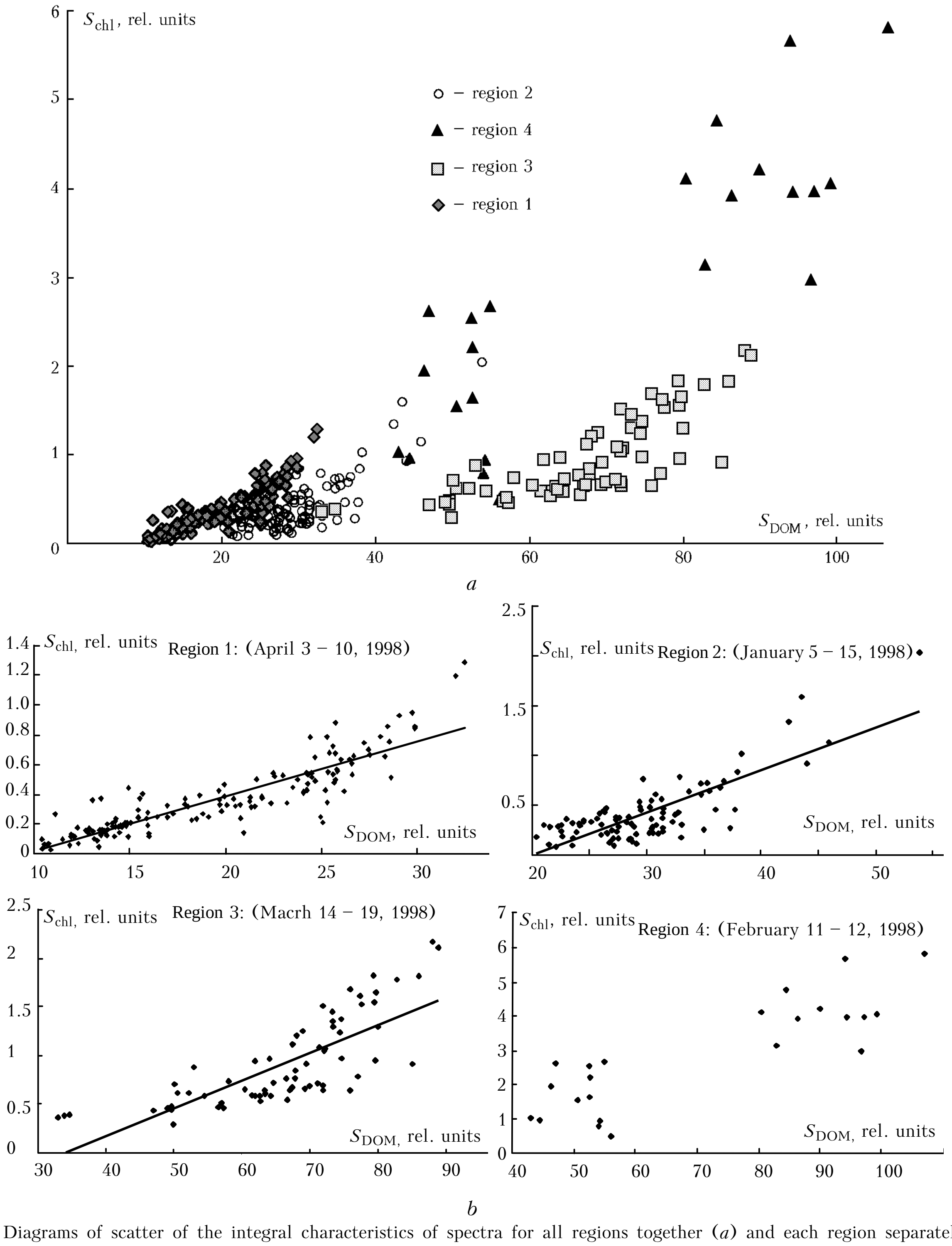

Fig. 3. Diagrams of scatter of the integral characteristics of spectra for all regions together (*a*) and each region separately (*b*). Pacific Ocean.

Similar situation was observed in the Sea of Okhotsk (see Fig. 2*b*). The diagram of scatter of S_{chl} and S_{DOM} is shown in Fig. 4. The scales of relative units in Figs. 3 and 4 differ widely, because different calibrations were used in these voyages to obtain the relative values of the parameters. In this case, as for the situation in the Tasmanian Sea, some correlation between the integral parameters of the fluorescence spectra of chlorophyll A and the dissolved organic matter can hardly be found. Clusterization of the results about two centroids with a wide scatter is observed. An attempt to separate the groups of measured data in different regions of the Sea of Okhotsk corresponding to some regression straight line failed as well. The Sea of Okhotsk is very complex from the viewpoint of dynamics of water masses carrying the organic matter. First of all, we should mention the outflow of the organic matter from the mouth of Amur River and upwelling zones, as well as the streams moving along the shelf zones of Sakhalin. Regardless of the relatively high concentration of chlorophyll A in the Sea of Okhotsk, these sources of organic matter are likely decisive in the formation of the background of the organic matter.

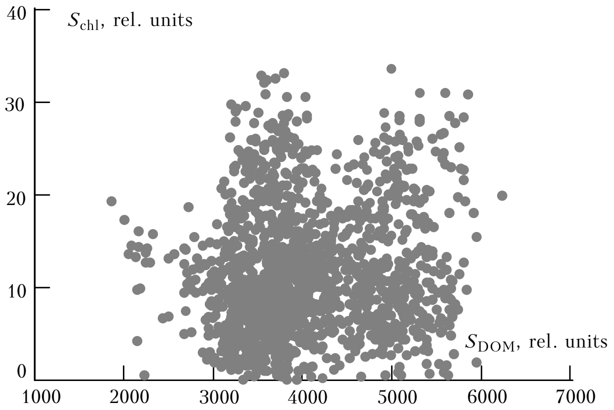

Fig. 4. Diagram of scatter of the integral spectral characteristics in the Sea of Okhotsk.

It should be emphasized that our analysis of the measured results refers only to those specific geophysical situations that occurred at the time of measurements. We should also keep in mind the possibility of the existence of weak correlation between the integral parameters of the florescence spectra of chlorophyll A and the dissolved organic matter in the cases that a great amount of various algae are in the water under study. Similar situation is also possible in the regions, where the species composition varies fast as the vessel goes. These two situations could take place at some sections of the route in the Sea of Okhotsk.

However, the considered method allows, first, applying the remote technique to determination of the correlation between the DOM and chlorophyll A (in the case of a lidar version of a laser fluorimeter). Second, what is most important, it allows us to introduce numerical relations that determine the degree of correlation between integral characteristics of the fluorescence spectra of chlorophyll A and the DOM (for example, using the value of the normalized rms deviations from the regression straight lines). Thus, some intermediate classes of seawater between the first and the second classes can be identified.

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