Some comparative results on chlorophyll *A* concentrations obtained in remote sensing of ocean color with the use of different two-band algorithms

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Some results are presented of the reconstruction of chlorophyll *a* concentration from the spectra of upwelling radiation from the sea depth. The results were obtained with the use of different two-band algorithms. The algorithms were applied to processing of experimental data obtained in some regions of the Pacific Ocean. Laser fluorimetry of seawater was performed simultaneously with the measurements of the spectra of upwelling radiation. The data of laser fluorimetry were used to assess the reliability of chlorophyll *a* concentration calculated by different two-band algorithms. Intercomparison of measured results has allowed us to determine new coefficients in the algorithm with cube polynomials for calculation of chlorophyll *a* concentration at which the values characterizing the difference between the obtained concentration and the data of laser fluorimetry are minimal.

1. Introduction

The spectrum of radiation upwelling from the sea depth bears the information about bio-optical characteristics of the seawater.[1,2] By now different empirical and semi-analytical algorithms have been developed which allow measurements of chlorophyll *a* concentrations in different regions of the Global Ocean from the spectral distribution of the sea surface reflectance.[3–6] The accuracy of reconstruction of the chlorophyll *a* concentration from the spectra of upwelling radiation depends on many factors. The main factor among them is the number of spectral channels for measuring the spectral distribution of the upwelling radiation. The large number of spectral channels allows one not only to accurately reconstruct the spectral dependence of the chlorophyll absorption coefficient,[7] but also to estimate the content of dissolved organic matter and suspended substances in the seawater.[8–10]

The use of satellite scanners with large number of spectral channels faces some technical difficulties. Thus, the CZCS scanner installed onboard the NASA Nimbus–7 satellite (in operation from October 1978 to July 1986) used four channels in the visible spectral region. The OCTS scanner (in operation from November 1996 to August 1997) onboard the NASDA ADEOS satellite had six bands in the visible spectral region. The now orbiting NASA Sea WiFS scanner also uses six spectral channels in the visible spectral region. To determine the chlorophyll *a* concentration, empirical algorithms are usually used. These algorithms employ the ratios among the reflectance of the sea surface in different spectral regions. The simplest among them are two-band algorithms which employ the ratio between the sea surface reflectance in two spectral intervals (in the blue–green region).[3] The most popular two-band "globalB (that is, used in a wide range of chlorophyll *a* concentration) algorithms borrowed from Ref. 11 are presented in Table 1.

Table 1

$C_1 = 10^{a_0+a_1R}$	$R = \log[R_{rs}(490)/R_{rs}(555)]$; $a_0 = 0.444$; $a_1 = -2.431$
$C_2 = 10^{a_0+a_1R+a_2R^2+a_3R^3}$	$R = \log[R_{rs}(490)/R_{rs}(555)]$; $a_0 = 0.45$; $a_1 = -2.86$; $a_2 = 0.996$; $a_3 = -0.3674$
$C_3 = 10^{a_0+a_1R_1+a_2R_2}$	$R_1 = \ln[R_{rs}(490)/R_{rs}(555)]$; $R_2 = \ln[R_{rs}(510)/R_{rs}(555)]$; $a_0 = 1.025$; $a_1 = -1.622$; $a_2 = -1.238$
$C_4 = 10^{a_0+a_1R}$	$R = \log[R_{rs}(443)/R_{rs}(555)]$; $a_0 = 0.2492$; $a_1 = -1.768$
$C_5 = 10^{a_0+a_1R}$	$R = \ln[R_{rs}(490)/R_{rs}(555)]$; $a_0 = 1.077835$; $a_1 = -2.542605$
$C_6 = 10^{a_0+a_1R+a_2R^2+a_3R^3}$	$R = \log[R_{rs}(443)/R_{rs}(555)]$; $a_0 = 0.207$; $a_1 = -1.828$; $a_2 = 0.758$; $a_3 = -0.739$
$C_7 = 10^{a_0+a_1R+a_2R^2+a_3R^3}$	$R = \log[R_{rs}(490)/R_{rs}(555)]$; $a_0 = 0.341$; $a_1 = -3.0$; $a_2 = 2.811$; $a_3 = -2.04$
$C_8 = 10^{a_0+a_1R+a_2R^2+a_3R^3}$	$R = \log[R_{rs}(443)/R_{rs}(565)]$; $a_0 = 0.438$; $a_1 = -2.114$; $a_2 = 0.916$; $a_3 = -0.851$

Note. R_{rs} are the experimentally measured values of the reflectance of the sea depth in the wavelength regions with centers indicated in parentheses; a_i are the corresponding regression coefficients; C_i are the chlorophyll *a* concentration values calculated by the *i*th formula.

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The empirical algorithms used the measured reflectance of the sea surfaces in more than two spectral bands to calculate the chlorophyll *a* concentration can be found, for example, in Refs. 12 and 13.

The above-listed two-band algorithms were developed based on calibration measurements for determining the regression coefficients, a_i. The choice of an algorithm, as well as the values of the regression coefficients, depends on the type of the seawater and the zone of measurements. To increase the accuracy, one should first determine the values of a_i from sub-satellite measurements, as it was done, for example, in Refs. 14 and 15. This is especially true for biological-matter-deficient oceanic waters with chlorophyll *a* concentration less than or about 0.05 μg/l, the Arctic and Antarctic waters, as well as those shelf waters, which fall in the second class. In these waters the indicated algorithms may give significant deviations from the actual chlorophyll *a* concentration.

In this paper we describe the results of shipborne measurements of the spectra of upwelling radiation from the sea depth. These measurements were conducted simultaneously with the laser fluorimetry measurements of the seawater in order to evaluate the applicability of the two-band algorithms proposed by NASA for reconstruction of the chlorophyll *a* concentration in the regions of the Pacific Ocean, where the use of two-band algorithms may face some difficulties. More specifically, these regions are the waters of the first class, but with chlorophyll *a* content at the level of hundredths microgram per liter, in the Antarctic waters, and the shelf waters of the second class.

2. Experimental setup and the region of measurements

The *in situ* measurements were conducted during the voyage of *Nadezhda* training sailing ship of the Far East State Marine Academy in the period from December 10, 1997, to April 20, 1998. The ship route is shown in Fig. 1.

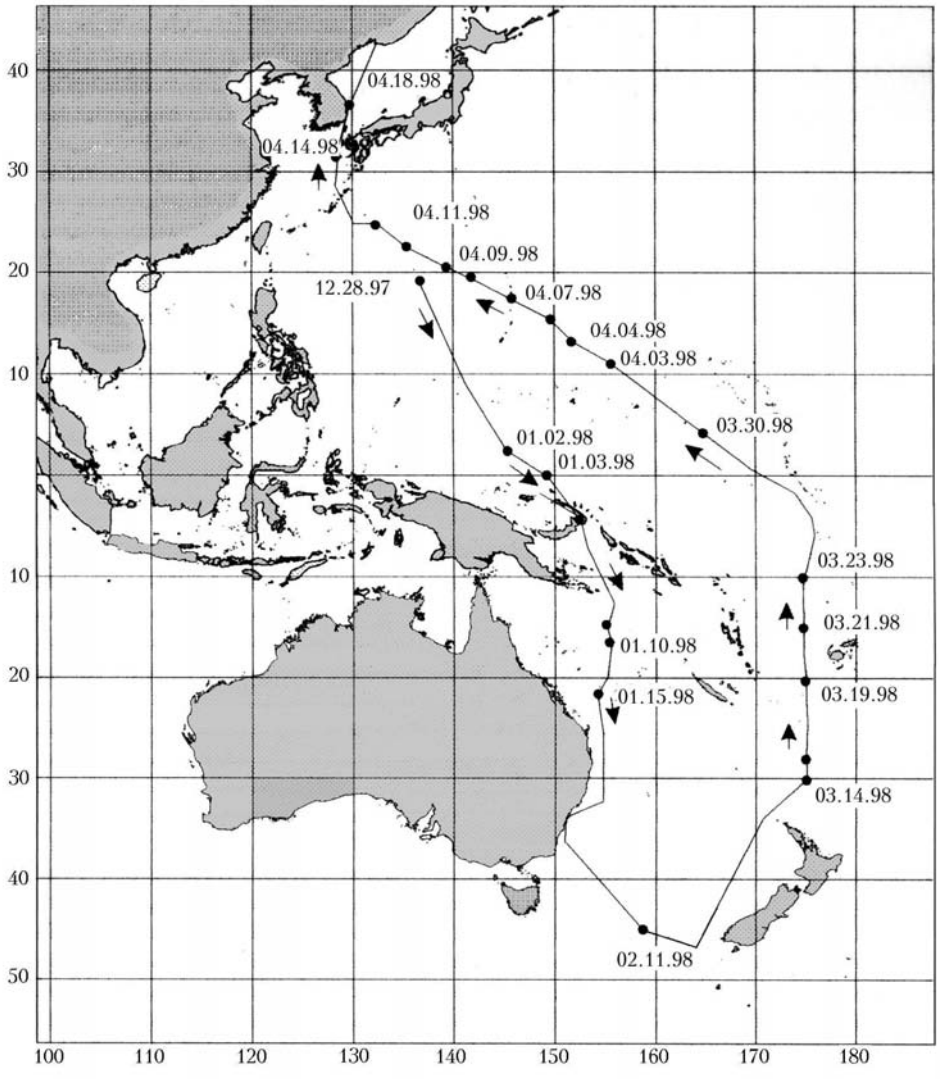

Fig. 1. The ship route during the voyage.

The circles in Fig. 1 denote the regions where we succeeded to conduct simultaneous measurements of both the spectrum of the upwelling radiation from the sea depth and the fluorescence spectra of the seawater along the ship path. The measurements were conducted in daytime in the period from 11:00 to 14:00, local time. The instrumentation comprised of a laser fluorimeter designed to measure the fluorescence spectra of the seawater, a polarization spectrometer to measure the spectra of the upwelling radiation, and a spectrophotometer to measure the chlorophyll *a* concentration in the sampled seawater by standard methods. The laser fluorimeter and polarization spectrometer allowed us to conduct the on-route measurements. The fluorescence was excited in the drawn-through cell; the scheme of the experiment is shown in Fig. 2.

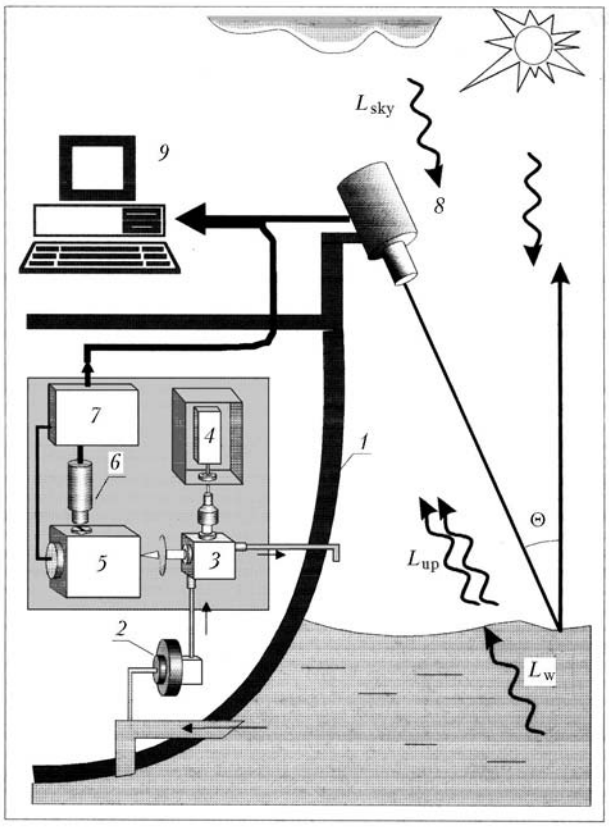

Fig. 2. The scheme of drawing-through the water and measurements of the fluorescence spectrum of the seawater: ship body (*1*); pump for water intake and drawing through the plastic pipe line (*2*); cell (*3*); the laser (*4*); scanning monochromator (*5*); photomultiplier tube (*6*); the ADC and monochromator control unit (*7*); a POLAS spectrometer (*8*); a computer (9).

To excite the fluorescence spectra, we used the second harmonic of a Nd:YAG laser at the wavelength of 532 nm, the pulse duration was about 20 ns, and the laser radiation energy per pulse did not exceed 10 mJ at the pulse repetition rate up to 10 Hz. The laser beam was expanded with a telescope up to 3 cm. The power density of laser radiation in the cell was about 70 kW/cm^2, thus ensuring the linear response of the fluorescence signal to laser excitation. Under these conditions, it is possible to determine the chlorophyll *a* concentration from the measured intensity of the fluorescence line at the wavelength of 675 nm using the method of internal benchmark.[16] According to this method, we measured the intensity ratio between the chlorophyll *a* fluorescence line at the wavelength of 675 nm and the Raman scattering line of liquid water at the wavelength of 645 nm (the spectral recording instrumentation allowed measurements of the fluorescence signal intensity in the region from 545 to 720 nm with the instrumental function 4 nm wide). This ratio was calibrated against the chlorophyll *a* concentration measured by the standard method from the absorption spectra. The concentration was measured in the sampled seawater taken from the cell. The calibration procedure was conducted only in the cases of possible change in the species composition of phytoplankton or in the regions with a wide spatial variability of phytoplankton concentration.

The cell contained 250 cm^3 of water. Water was drawn through the specialized plastic pipeline, which provided for water intake from the depth of about 4 m; the drawing-through rate was 2 l/min. The spatial resolution was governed by the processing time for the fluorescence spectrum. Obtaining the whole spectrum from 545 to 720 nm took one minute at a 4-nm wide instrumental function. As the ship moves with the speed about 8 knots, the spatial resolution was 240 m. Three spectra sequentially measured along the ship route are shown in Fig. 3. In Fig. 3 the wavelength, in nanometers, is plotted as the horizontal axis, and the fluorescence signal intensity is plotted as the vertical axis. The spectrum corresponds to the mean concentration of chlorophyll *a* about 0.4 μg/l.

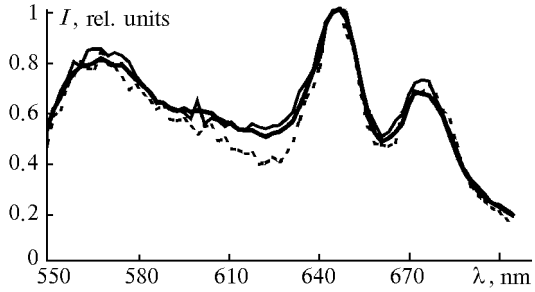

Fig. 3. Fluorescence spectra of the sea water.

The spectral composition of the radiation upwelling from the sea depth was measured with the use of a POLAS polarization spectrophotometer. The measured parameters were the following: brightness of the upwelling radiation L_{up}, sky brightness L_{sky}, brightness of the radiation reflected from the standard diffuse scattering screen L_r, which was determined once a day before starting the measurement session. In Fig. 2 L_w is the underwater brightness of the upwelling radiation. The spectrometer was installed at the altitude of 7 m above the sea level, the angle θ_m was

about 45°. The polarizer recording only *P*-components of the upwelling radiation was set in front of the entrance objective of the spectrophotometer. Such a scheme ensured minimal contribution of the *P*-component of the sky background reflected from the sea surface to the intensity of radiation upwelling from the sea depth. Below we present the specifications of the polarization spectrophotometer used.

Spectral range of measurements	425–800
Number of recording signals (vertical polarization)	1
Number of spectral channels	200
Measurement time (200 points), s	4
Dynamic range of the measured signal, dB	70
Field-of-view angle, degs.	2
Spectral resolution, nm	2

Figure 4 shows typical spectrum of the upwelling radiation recorded with the POLAS spectrometer.

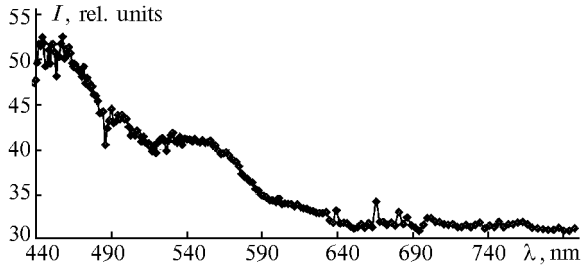

Fig. 4. Example of spectral distribution of the upwelling radiation.

The large number of channels available in measurements allowed us to use not only two- or three-band algorithms for reconstructing the chlorophyll *a* concentration, but also the methods of multichannel processing of the obtained results.[7] Below we present only the results of data processing using the two-band methods.

3. Analysis of the experimental results

All measurements were conducted in the Pacific Ocean the waters of which were divided into four regions according to their bio-optical characteristics. The first three regions fall in the category of optical waters of the first class and differ only by the mean concentration of phytoplankton. The first region was the organic-matter-deficient waters of the Pacific Ocean, which are close to the shelf waters (the circles in Fig. 1 for the period from December 28, 1997, to January 15, 1998). The second region was the Antarctic waters with high content of phytoplankton (February 11, 1998). The third region was in the open waters of the Pacific Ocean (March 14 – April 11, 1998); and the fourth region (in the shelf waters of the Japan Sea) was classified as the waters of the second class (April 18, 1998). The mean values of the chlorophyll *a* concentration for each region determined from the data of laser fluorimetry were respectively 0.06, 0.3, 0.03, and 0.7 μg/l.

The measurement data acquired with the POLAS spectrometer and with the laser fluorimeter in these regions were subjected to identical pre-processing. They were averaged over the same time interval and filtered. Then the chlorophyll *a* concentration was calculated from the array of R_s values obtained in this way with the use of the empirical formulas given in Table 1. The time interval of averaging (10 min) corresponded to the spatial averaging about 2 km.

The values given by the laser fluorimetry were taken as "trueB values of chlorophyll *a* concentration in the given regions. The chlorophyll *a* concentration values obtained with the use of eight different two-band algorithms were compared with those acquired by the laser fluorimetry for the same region and during same time interval.

Such a spatial averaging smoothes out the fluctuations of concentration due to the spotted structure of phytoplankton field in the upper surface layer. This circumstance allows us to avoid the discussion of different measurement methods of the chlorophyll *a* concentration from the spectra of upwelling radiation (in this case the results are averaged over the area of the sea surface which falls into the field of view of the receiving optics) and by the method of laser fluorimetry, where the concentration is determined at the depth about 4 m along the averaging path. This problem is associated with manifestation of different scales in spatial inhomogeneities of the chlorophyll *a* distribution and calls for separate investigation. Here we only would like to note that in the regions with the pronounced spotted structure (the second and fourth regions) the correlation coefficients between the chlorophyll concentration distributions constructed from the data of laser fluorimetry and spectral measurements of the upwelling radiation depended strongly on the spatial averaging and were insignificant at minimal spatial resolution of 240 m. This fact can be explained by different influence of small-scale variability in the horizontal distribution of phytoplankton on the results of measurements conducted with the use of different methods.

To assess, which of the eight algorithms presented in Table 1 gives the chlorophyll *a* concentration closest to that given by laser fluorimetry, we calculated, for each region, the following parameters: rms deviation of each concentration value determined using the formulas from Table 1 from the value obtained in fluorimetric measurements S_d, the mean absolute value of the deviation M_d, the maximum absolute value of the deviation Max:

$$S_d = \sqrt{\frac{\Sigma(C_{fi} - C_i)}{N-1}}\,;\; M_d = \frac{\Sigma\,|C_{fi} - C_i|}{N}\,;$$
$$\mathrm{Max}\,|C_{fi} - C_i|\,,$$

where C_{fi} are the values of concentration obtained from fluorimetric measurements; C_i are the concentration values obtained with the use of the POLAS spectrometer; the results are summed over all measurements conducted in each region considered.

Table 2

Algorithm	Region											
	first			second			third			fourth		
	0.06 μg/l			0.3 μg/l			0.03 μg/l			0.7 μg/l		
	S_d	M_d	Max	S_d	M_d	Max	S_d	M_d	Max	S_d	M_d	Max
C_1	0.35	0.37	2.05	0.22	0.23	0.86	0.40	0.35	1.73	0.40	0.65	1.41
C_2	0.32	0.37	1.99	0.19	0.21	0.77	0.35	0.35	1.65	0.40	0.58	1.32
C_3	0.34	0.32	1.68	0.24	0.16	0.87	0.39	0.26	1.70	0.53	0.80	1.55
C_4	0.27	0.31	1.09	0.21	0.18	0.92	0.28	0.22	1.26	0.40	0.53	1.15
C_5	0.37	0.29	1.57	0.32	0.19	1.43	0.41	0.22	1.89	0.68	1.04	2.11
C_6	0.23	0.31	0.99	0.19	0.17	0.81	0.26	0.22	1.13	0.37	0.45	1.02
C_7	0.22	0.61	1.48	0.11	0.30	0.62	0.56	0.79	3.05	0.31	0.34	0.93
C_8	0.38	0.45	1.65	0.31	0.34	1.49	0.42	0.33	1.90	0.56	1.09	1.94

The calculated data for the four regions are given in Table 2.

As seen from Table 2, all the three parameters have large values relative to the mean concentration ones C_{fi} no matter what algorithm is used. Especially large are the maximum deviations from C_{fi}. Thus, for the mean concentration about hundredths microgram per liter (the first and third regions), the maximum deviations reach several micrograms per liter. This supports the fact that "globalB algorithms give highly overestimated values at concentrations less than 0.05 μg/l.

It should be noted that the first and fourth regions also fall in the category of extreme regions, where the algorithms $C_1 - C_8$ with the above-indicated regression coefficients give overestimated concentration values. The data obtained open up the possibility of constructing new regression formulas similar to the algorithms $C_1 - C_8$. We selected suitable coefficients for the algorithms of the type $C = 10^{a_0+a_1R+a_2R^2+a_3R^3}$, where $R = \log[R_{rs}(490)/R_{rs}(555)]$.

The new values of coefficients a_i and the values of S_d, M_d, and Max corresponding to the concentration values found with the use of these coefficients are given in Table 3.

Table 3

Region	a_0	a_1	a_2	a_3	S_d	M_d	Max
1	−1.123	0.381	−2.686	0.647	0.03	0.02	0.07
2	0.210	4.032	11.829	11.033	0.05	0.04	0.11
3	−0.714	−2.955	3.775	−1.333	0.02	0.02	0.06
4	0.106	−5.167	39.095	− 110.94	0.24	0.21	0.47

One can see from comparison of data presented in Tables 2 and 3 that the values of S_d, M_d, and Max decreased in some cases by more than order of magnitude due to the selection of new regression coefficients.

Thus, our experimental measurements in the regions of the Pacific Ocean in waters of the first class with low chlorophyll content (less than or about 0.05 μg/l) and in the Antarctic and shelf waters of the second class support that "globalB empirical two-band algorithms may give overestimated concentrations of chlorophyll *a*. When measuring the chlorophyll *a* concentration in such regions, one should at least select suitable values of the coefficients in these empirical algorithms. These coefficients depend on particular values of the bio-optical characteristics of the waters under study.

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