ESTIMATION OF CHLOROPHYLL CONCENTRATION IN SEA WATER FROM MEASUREMENTS OF SPECTRAL INDEX OF VERTICAL LIGHT EXTINCTION

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The technique has been proposed for calculating the concentration of main constituents of impurities contained in the sea water, which does not require a priori *information about the sea water type. It is shown that when variations of main parameters of sea water absorption model and of input parameters are no more than 10%, the error in estimation of the chlorophyll concentration will be no more than 20–25%. The results obtained using this technique have been compared with the direct measurements of chlorophyll concentration.*

The determination of chlorophyll content in the sea water is an important problem in evaluating the level of phytoplankton primary production, global fluxes of matter and energy, and monitoring of various areas of the World Ocean in the interests of ecology and fishing.[1–3]

As known, the methods for measurement of the index of vertical light extinction in the ocean α and the coefficient of diffuse light reflection by the ocean R have been well developed.[1] Therefore, the estimation of concentration of main constituents of impurities contained in the sea water, namely, chlorophyll, DOYM (dissolved organic yellow matter), and suspended matter from such measurements may be highly efficient. In this paper we propose the method for estimating the chlorophyll concentration from the multispectral measurements of α and R without *a priori* information about the sea water type, including measurements in waters of shelf, shallows, etc.

Our calculation was done in two steps. At the first step, from the measured values of the spectral index of vertical light extinction $\alpha_{\lambda i}$ and coefficient of diffuse light reflection $R_{\lambda i}$, ($i = 1,\ldots, N$ is the number of spectral measurements) the values of the index of light absorption by water $\varkappa_{\lambda i}$ were found. At the second step, such values of the chlorophyll concentration and the absorption index of DOYM and suspended matter were chosen that would provide the closest possible approach to the obtained spectral dependence of the total absorption index.

1. DETERMINATION OF THE ABSORPTION INDEX $\varkappa_{\lambda i}$ FROM THE INDEX OF VERTICAL LIGHT EXTINCTION $\alpha_{\lambda i}$

As known, the spatial density of light energy absorption by an elementary volume is equal to divergence of the vector of light energy transfer **H**:

$$\varkappa E^\circ = -\mathrm{div}\,\mathbf{H}, \qquad (1)$$

where $\varkappa$ is the index of light absorption by water, E° is the spatial illuminance of the given volume ($E^\circ = \int_{4\pi} B \mathrm{d}\omega$, where B is the brightness). Since horizontal gradients of optical properties of water are much smaller than vertical ones (vertically stratified medium) and the scale of nonuniformity in surface illumination by daylight far exceeds the scale of vertical variability of light field in water, the horizontal gradients of **H** can be neglected. The vertical component of the vector, H_z, equals the difference between illuminance of elementary volume from the top ($E_\downarrow$) and bottom ($E_\uparrow$). Then Eq. (1) takes the form

$$\frac{\mathrm{d}(E_\downarrow - E_\uparrow)}{\mathrm{d}z} = -\varkappa E^\circ. \qquad (2)$$

Having divided Eq. (2) by $(E_\downarrow - E_\uparrow) = E_\downarrow(1 - R)$, where R is the coefficient of diffuse light reflection by sea, we derive the formula

$$\alpha\left[1 + \frac{\mathrm{d}R/\mathrm{d}z}{\alpha(1 - R)}\right] = \varkappa\,\frac{E^\circ}{E_\downarrow - E_\uparrow}. \qquad (3)$$

In Eq. (3), $\alpha = 1/E_\downarrow[\mathrm{d}E_\downarrow/(\mathrm{d}z)]$ is the index of vertical light extinction for downward light radiation flux. The parameter R varies only slightly with depth. The processing of experimental data has shown[1] that the second term in brackets is no more than 0.04; therefore, it can be ignored. In the right-hand side of Eq. (3) there is the expression for the mean cosine of the angle of the radiation incidence:

$$\frac{E_\downarrow - E_\uparrow}{E^\circ} = \frac{\int_{4\pi} B\cos\theta\, \mathrm{d}\omega}{\int_{4\pi} B \mathrm{d}\omega} = \mu_\circ, \qquad (4)$$

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where θ is the angle between the vector of brightness and the downward normal. Then the formula for calculation takes the form[4]:

$$\varkappa = \alpha\mu\,. \tag{5}$$

As has been shown in the course of model experiment and measurements carried out in the Indian Ocean,[5] the mean cosine of the angle of the incidence is highly correlated with the coefficient of diffuse reflection according to the equation of regression

$$\mu = 1 - 0.185\sqrt{R} \tag{6}$$

(where R is in per cent). The error in determining μ using this formula is small ($\mu^{+0.04}_{-0.03}$). The values of R can be found from direct measurements. When researches are conducted outside the shelf zones of the World Ocean, the typical values of R can be used[1] depending on the experimental value of α_{500} (index of vertical light extinction at 500 nm).

So, from measured α_λ and R_λ the coefficient $\varkappa_\lambda$ of sea water can be found using Eqs. (5) and (6). Since α and R can be measured at different depths, in this way we can obtain the depth profile of $\varkappa_\lambda$.

2. METHOD FOR CALCULATING THE CHLOROPHYLL CONCENTRATION AND THE ABSORPTION INDICES OF DOYM AND SUSPENDED MATTER

Let us assume that the index of light absorption by the sea water is the sum of four terms

$$\tilde{\varkappa}_\lambda = \varkappa_{\omega,\lambda} + C_{\rm ch}\,\varkappa^*_{{\rm p},\lambda}(C_{\rm ch}) + \varkappa_{\rm ys}\exp\{-g(\lambda-\lambda_0)\} + \varkappa_{\rm sm}\,. \tag{7}$$

Here, $\varkappa_{\omega,\lambda}$ is the index of light absorption by clear water; $C_{\rm ch}$ is the chlorophyll concentration, in mg/m^3; $\varkappa^*_{{\rm p},\lambda}$ is the index of specific absorption by phytoplankton pigments depending on the chlorophyll concentration; $\varkappa_{\rm ys}$ is the index of light absorption by yellow matter at a wavelength λ_0; and, $\varkappa_{\rm sm}$ is the index of light absorption by suspended particles, without regard for phytoplankton pigments. The tilde atop the symbol in Eq. (7) means that this absorption index is model.

Let the indices $\varkappa_{\lambda_i}$ ($i = 1, \ldots, N$) be obtained from measurements of the index of vertical light extinction and the coefficient of diffuse reflection and calculations according to the procedure described Section 1. To find the concentration of impurities providing most close approach to these $\varkappa_{\lambda_i}$, we will search for the minimum of the goal function

$$P_\Sigma = \sum_{i=1}^{N} (\varkappa_{\lambda_i} - \tilde{\varkappa}^2_{\lambda_i}) \tag{8}$$

in 3D space of parameters with coordinates $x = C_{\rm ch}$, $y = \varkappa_{\rm ys}$, and $z = \varkappa_{\rm sm}$. In fact, this means the choice of such values of impurity concentration that provide minimum deviation of $\tilde{\varkappa}_\lambda$ from the experimental data. The function P_Σ is the quadratic form in y and z.

Setting the derivatives with respect to y and z equal to zero, we obtain the system of two equations linear in y and z:

$$\begin{cases} \sum\limits_{i=1}^{N} (x\varkappa^*_{{\rm p},\lambda}(x) + y{\rm e}^{-g(\lambda_i-\lambda_0)} + z - (\varkappa_{\lambda_i} - \varkappa_{\omega,\lambda_i}))\ {\rm e}^{-g(\lambda_i-\lambda_0)} = 0, \\ \sum\limits_{i=1}^{N} (x\varkappa^*_{{\rm p},\lambda}(x) + y{\rm e}^{-g(\lambda_i-\lambda_0)} + z - (\varkappa_{\lambda_i} - \varkappa_{\omega,\lambda_i})) = 0. \end{cases} \tag{9}$$

Having solved this system for y and z, we can find the parameters $y_{\rm min}(x)$ and $z_{\rm min}(x)$ which provide the minimum of the goal function P_Σ for given x. After substitution of the derived expressions into Eq. (8), the goal function transforms into the function of a single variable $P^{\rm mod}_\Sigma(x)$. Since it is not quadratic in x, the method of golden section[6] is used to search for its minimum. The algorithm for estimating the concentration of chlorophyll and other impurities is constructed in the following way. After input of model parameters and $\varkappa_{\lambda_i}$, the interval of values of chlorophyll concentration is set at which the minimum of the modified goal function $P^{\rm mod}_\Sigma(x)$ will be sought for as well as the accuracy of $x_{\rm min}$ estimation. Then the search for $x_{\rm min}$ is conducted by the method of golden section, and for the given $x_{\rm min}$ the values of $y_{\rm min}$ and $z_{\rm min}$ are then computed.

When using the methods of golden section, the function $P^{\rm mod}_\Sigma(x)$ should be computed repeatedly. To this end, the dependence of the index of specific absorption by phytoplankton pigments $\varkappa^*_{\rm p}$ on the chlorophyll concentration must be known. In Ref. 6, as a result of statistical processing of experimental data, the following expression was derived for the dependence of the index of specific light absorption by phytoplankton pigments on the pigment chromaticity $C_{\rm pc}$:

$$\begin{aligned} \varkappa^*_{{\rm p},\lambda} &= (1.87\cdot10^{-2}C_{\rm pc} - 1.10\cdot10^{-2}) \times \\ &\times \exp\{-1.2\cdot10^{-4}(\lambda-441)^2\} + \\ &+ 6.45\cdot10^{-3}\exp\{-3.3\cdot10^{-4}(\lambda-608)^2\} + \\ &+ 2.33\cdot10^{-2}\exp\{-1.44\cdot10^{-3}(\lambda-675)^2\}, \end{aligned} \tag{10}$$

where $C_{\rm pc} = \varkappa^*_{{\rm p},443}/\varkappa^*_{{\rm p},661}$.

The pigment chromaticity $C_{\rm pc}$ in its turn depends on the chlorophyll concentration $C_{\rm ch}$ in a way shown in Fig. 1 (Ref. 7). The corridor of possible values of $C_{\rm ch}$ is shown in Fig. 1. The values used in the algorithm for a spline approximation of this dependence are marked.

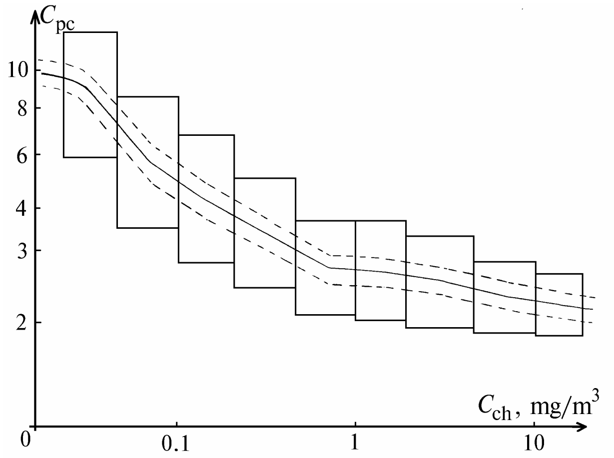

FIG. 1. Pigment chromaticity as a function of the chlorophyll concentration. The corridors of possible values of C_{ch} and C_{pc} are shown. Solid line is for approximation used in the algorithm for calculating C_{ch}, and dashed lines show the function at 10% change in chromaticity.

3. CALCULATION OF C_{ch}, $\varkappa_{ys}$, AND $\varkappa_{sm}$ USING THE PROPOSED TECHNIQUE. INFLUENCE OF THE ACCURACY OF MEASUREMENTS AND PRESET PARAMETERS ON THE ACCURACY OF ESTIMATES

As an example, the proposed technique was used for calculating the chlorophyll concentration in oligotrophic and eutrophic waters. The indices of vertical light extinction averaged over a large number of measurements and used previously for optical classification of oceanic waters[8,9] served as the initial data. Table I presents the values of α_λ corresponding to the optical refractive indices $m = 2$ (oligotrophic waters) and 5 (eutrophic waters) according to this classification, as well as the values of $\varkappa_\lambda$ calculated by formulas (5) and (6). Taken as the index of light absorption by clear water was the value of $\varkappa_\lambda$ for $m = 1.15$, which is the minimum value of the optical refractive index m ever observed in the World Ocean (this extremely small value of m was measured in the Caribbean Sea[10]).

Then using the values of $\varkappa_\lambda$ from Table I and calculating by the algorithm described in Section 2, the following results were obtained:

– in oligotrophic waters at $m = 2$, the chlorophyll concentration $C_{ch} = 0.136$ mg/m^3, the DOYM absorption index $\varkappa_{ys}(\lambda = 500\,\text{nm}) = 1.67 \cdot 10^{-3}\,\text{m}^{-1}$, and the suspended matter absorption index $\varkappa_{sm} = 5.88 \cdot 10^{-3}\,\text{m}^{-1}$;

– in eutrophic waters at $m = 5$, $C_{ch} = 1.015$ mg/m^3, $\varkappa_{ys} = 1.06 \cdot 10^{-2}\,\text{m}^{-1}$, and $\varkappa_{sm} = 3.42 \cdot 10^{-2}\,\text{m}^{-1}$.

Shown in Fig. 2 are corresponding spectra of light absorption by the three constituents of impurities and the gross spectrum of absorption by the sea water. Marked by circles are the values of $\varkappa_\lambda$ from Table I, which were used in calculations.

TABLE I. Spectral dependence of the indices of vertical light extinction and absorption by the sea water.

λ, nm	Waters			
	Oligotrophic, $m = 2$		Eutrophic, $m = 5$	
	α	ϰ	α	ϰ
350	0.072	0.043	0.229	0.177
360	0.067	0.040	0.210	0.162
380	0.059	0.036	0.184	0.142
400	0.054	0.034	0.170	0.131
420	0.051	0.032	0.160	0.123
440	0.049	0.032	0.151	0.117
460	0.046	0.031	0.138	0.107
480	0.042	0.028	0.122	0.093
500	0.045	0.032	0.113	0.086
520	0.060	0.046	0.119	0.092
540	0.067	0.053	0.120	0.092
560	0.086	0.069	0.137	0.107
580	0.116	0.096	0.168	0.134
600	0.201	0.170	0.253	0.208

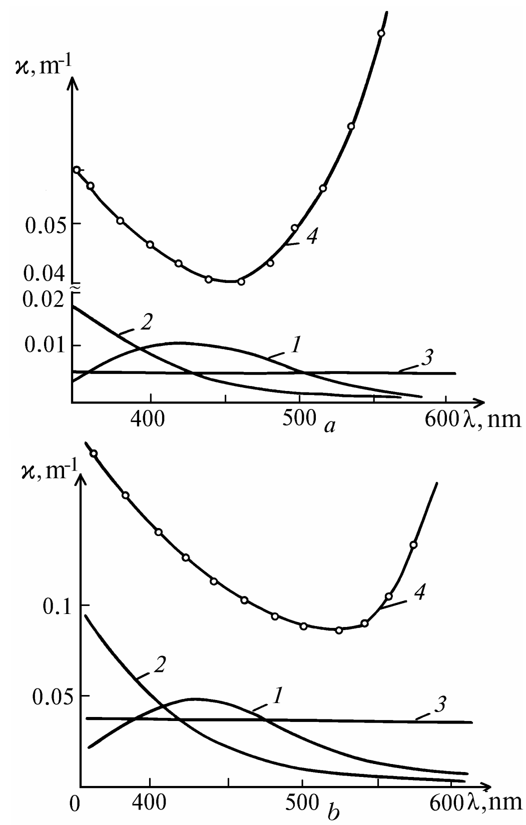

FIG. 2. Spectra of light absorption by constituents of impurities and the gross spectrum of light absorption by the sea water obtained by optimization for oligotrophic waters with $m = 2$ (a) and eutrophic waters with $m = 5$ (b): the index of light absorption by phytoplankton pigments (1), the index of light absorption by DOYM (2), the index of light absorption by suspended matter without regard for pigments (3), and the total index of light absorption by the sea water.

Let us now estimate the stability of the result obtained with respect to the employed assumptions. For this model of absorption, the parameter $g = 0.015$ nm^{-1} borrowed from Ref. 11 was used. As was shown in Ref. 11, the value of g varies within 10% of this value. To estimate the influence of such variations upon the result, we made calculations at $g = 0.014$ and 0.016. The deviations obtained are listed in Table II. As seen, the value of g influences mainly $\varkappa_{ys}$, whereas the calculated value of C_{ch} varies within 6%.

TABLE II. Error in estimation of C_{ch}, $\varkappa_{ys}$, and $\varkappa_{sm}$ for 10% variation of model and input parameters.

Mean value	Variable parameters		
	g	C_{pc}	$\varkappa_\lambda$
$m = 2$			
$C_{ch} = 0.136$	±0.008	±0.026	±0.020
$\varkappa_{ys} = 0.167\cdot10^{-2}$	$\pm0.027\cdot10^{-2}$	$\pm0.01\cdot10^{-2}$	$\pm0.011\cdot10^{-2}$
$\varkappa_{sm} = 0.588\cdot10^{-2}$	$\pm0.007\cdot10^{-2}$	$\pm0.01\cdot10^{-2}$	$\pm0.070\cdot10^{-2}$
$m = 5$			
$C_{ch} = 1.015$	±0.06	±0.15	±0.08
$\varkappa_{ys} = 0.165\cdot10^{-2}$	$\pm0.17\cdot10^{-2}$	$\pm0.01\cdot10^{-2}$	$\pm0.04\cdot10^{-2}$
$\varkappa_{sm} = 3.42\cdot10^{-2}$	$\pm0.04\cdot10^{-2}$	$\pm0.05\cdot10^{-2}$	$\pm0.28\ 10^{-2}$

Inaccurate knowledge of the dependence of pigment chromaticity on the chlorophyll concentration may be the other source of error. Our estimates of the influence of this dependence upon the result obtained by the given algorithm have shown that when the chromaticity is changed by 10% (dashed curves in Fig. 1), which is equal to about 1/3 of the maximum deviation, the result changes as shown in Table II, and C_{ch} is changed most markedly, up to 15–20%.

Influence of the error in determination of α_λ and hence $\varkappa_\lambda$ upon the result of calculation of C_{ch}, $\varkappa_{ys}$, and $\varkappa_{sm}$ was estimated by modeling of random deviations of $\varkappa_\lambda$ from its average value with the coefficient of variation being equal to 10% ($\varkappa_\lambda$ can be determined with such accuracy in the selected spectral range due to sufficiently high accuracy of measurement of α_λ). This error turned out to influence most strongly the value of $\varkappa_{sm}$ (see Table II).

Thus, variations of model and input parameters within 10% produce the error in estimation of C_{ch}, $\varkappa_{ys}$ and $\varkappa_{sm}$ no more than 20–20%.

4. COMPARISON OF CALCULATED RESULTS WITH DIRECT MEASUREMENTS

The index of vertical light extinction and the concentration of chlorophyll measured by us in 1991 from onboard the research ship *Vityaz'* were used for the comparison with the results of C_{ch} calculations by the proposed technique. The processing of data for several stations has shown that at $\alpha_{500} = 0.045$ ($m = 2$) the mean chlorophyll concentration was 0.17 mg/m^3, which differs by 23% from the calculated result $C_{ch} = 0.136$ mg/m^3. At $\alpha_{500} = 0.113$ ($m = 5$), the mean chlorophyll concentration was 0.87 mg/m^3, i.e., by 14% less than the calculated value $C_{ch} = 1.015$ mg/m^3, which falls within the above-indicated error in estimation of C_{ch}.

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