Modelling the influence of acclimation on the absorption properties of marine phytoplankton*

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Abstract

An algorithm for calculating the marine phytoplankton total spectral absorption coefficient and its components for particular groups of photosynthetic and photoprotecting pigments has been developed. The input data for the calculations are the concentrations of these groups of pigments and depth in the sea. Over 1400 sets of simultaneously measured phytoplankton absorption properties and pigment contents at different depths in various water types were applied in the modelling. Photo- and chromatic acclimation as well as the package effect of pigments in cells and its variation in different waters have been considered. The vertical profiles of the product $C_I\,d$ are also described.

1. Introduction

Models of the specific spectral absorption coefficient of chlorophyll *a* in living marine phytoplankton $a^*_{pl}(\lambda)$ constructed hitherto have usually taken account of its dependence on the chlorophyll concentration C_a in the sea (see *e.g.* Woźniak & Ostrowska 1990, Woźniak *et al.* 1992a,b, Bricaud *et al.* 1995). However, these models do not consider the variability of plankton absorption coefficients due to photo- and chromatic acclimation of the plankton cells. The acclimation effects causes the pigment composition to vary (Woźniak *et al.* 1997) and in consequence a large variation in $a^*_{pl}(\lambda)$ which, therefore, differ in different geographical zones and depths in the sea (Koblentz-Mishke *et al.* 1995, Babin *et al.* 1996, Morel *et al.* 1996, Allali *et al.* 1997).

The main aim of the present work was, therefore, to construct a model description of the coefficient $a^*_{pl}(\lambda)$ which takes the adaptive effect into consideration. A further aim was to calculate the portion of light absorption in the total absorption $a^*_{pl}(\lambda)$ by the following pigment groups:

- non-photosynthetic (photoprotecting) pigments (PPP), $a^*_{PPP}(\lambda)$,
- all photosynthetic pigments (PSP), $a^*_{PSP}(\lambda)$, and
- part of the photosynthetic pigments (PSP, f_c) connected with the functional PS2 reaction centres only, $a^*_{PSP,\,f_c}(\lambda)$.

As has been shown in Woźniak *et al.* (1997) and Majchrowski (1999), there exist approximate relationships between the light conditions in the sea and the phytoplankton pigment composition (photosynthetic and non-photosynthetic). To achieve the above aims, mathematical formulae (algorithms) to determine the absorption coefficients $a^*_{pl}(\lambda)$ as a function of specific absorption coefficients and concentrations of the component phytoplankton pigments should be established. The package effect influencing the observed values of the phytoplankton absorption coefficients (Morel & Bricaud 1981) should also be taken into consideration. In addition, the ratio of the number of functional reacting centres to the total number of centres should be included.

The model equations suitable for describing the set of absorption coefficients can be simply written as follows:

$$a^*_{pl}(\lambda) = a^*_{pl,S}(\lambda)\, Q^*(\lambda), \tag{1}$$

$$a^*_{PPP}(\lambda) = a^*_{PPP,S}(\lambda)\, Q^*(\lambda), \tag{2}$$

$$a^*_{PSP}(\lambda) = a^*_{pl}(\lambda) - a^*_{PPP}(\lambda), \tag{3}$$

$$a^*_{PSP,f_c}(\lambda) = a^*_{PSP}(\lambda)\, f_c, \tag{4}$$

where the index S denotes 'in solvent' and the package effect spectral function is

$$Q^*(\lambda) = \frac{3}{2\rho'(\lambda)}\left[1 + \frac{2\,e^{-\rho'(\lambda)}}{\rho'(\lambda)} + 2\,\frac{e^{-\rho'(\lambda)} - 1}{\rho'^2(\lambda)}\right], \tag{5}$$

and

$\rho' = a^*_{pl,S}\, C_I\, d$, according to van de Hulst (1981), on the assumption that phytoplankton cells are optically soft particles (Morel & Bricaud 1981);

f_c – portion of functional PS2 reaction centres;

C_I – intercellular chlorophyll a concentration;

d – cell diameter.

All these symbols, as well as the ones not explained in the text, are given in Appendix 1.

The main problem in the application of this simple model is that the respective absorption coefficients in solvent, *i.e.* of the 'unpackaged' pigments, are complex sums of absorption coefficients of particular photosynthetic and photoprotecting pigments:

$$\begin{aligned} a^*_{pl,S}(\lambda) = &\frac{1}{C_a}\Big[C_a\ a^*_a(\lambda) + C_{PSC}\ a^*_{PSC}(\lambda) + C_b\ a^*_b(\lambda)\ + \\ &+\ C_c\ a^*_c(\lambda) + C_{PPC}\ a^*_{PPC}(\lambda)\Big], \end{aligned} \tag{6}$$

$$a^*_{PPP,S}(\lambda) = \frac{1}{C_a}\Big[C_{PPC}\ a^*_{PPC}(\lambda)\Big]. \tag{7}$$

It should be noted that the 'unpackaged' specific absorption coefficient, *i.e.* in solvent, for component groups of pigments a^*_a, a^*_b, a^*_c, a^*_{PSC}, a^*_{PPC} are expressed in m^2 per unit of mass of the particular pigment (that is, not per unit of mass of chlorophyll a).

The specific absorption coefficients of the component pigments in eqs. (6) and (7) have unfortunately not been determined uniformly (*e.g.* Bidigare *et al.* 1990, Hoepffner & Sathyendranath 1991). Moreover, the products $C_I\, d$, which determine the package effect, are unknown and variable in different seas and at various optical depths τ. The portion of functional centres

f_c is also undetermined. Application of the model described by formulae (1)–(7) therefore requires the specific light absorption coefficient spectra to be determined for both photosynthetic and photoprotecting pigments. Likewise, the typical values of the products $C_I\,d$ and the functional PS2 reaction centres portion f_c for waters of different trophicity and at various depths in the sea have to be found.

2. Methods and materials

Initially, the problems stated above were solved in the following way. Numerous absorption coefficient spectra $a_{pl}(\lambda)$ and individual phytoplankton pigment concentrations obtained empirically from various seas and various optical depths were collected and applied as input data (Table 1). They come mainly from two sources: one is the common Polish–Russian database and the second is the ULISSE[1] campaign. The first contains the results of the voyages of r/v 'Vityaz', r/v 'Mendeleev', r/v 'Professor Shtokman', r/v 'Akademik Kurchatov', r/v 'Profesor Siedlecki', r/v 'Oceania' to all the oceans in the 1970s, 80s and 90s (Vinogradov 1971, 1980, Koblentz-Mishke *et al.* 1985, Koblentz-Mishke & Belayeva 1987, Konovalov *et al.* 1990), as well as the data from the SOPOT′87 Experiment (Woźniak 1991). The ULISSE experiment was carried out in the Baltic Sea in 1993–1994 (Ooms 1996).

The spectra of $a_{pl}(\lambda)$ of about 1400 samples of phytoplankton were examined. The determination of $a_{pl}(\lambda)$ was done by measuring the absorption of phytoplankton samples collected on filters. During joint Polish–Russian measurements, spectrophotometers equipped with a large integrating sphere, which allows the filter to be placed in the middle of the sphere, were applied. Konovalov (1992) elaborated the equations for the β factor for various filter types, which were used during many years of measurements. He also took into account the fact that the filters were sometimes initially covered (before filtration) with a $BaCO_3$ layer, and found the β factor for such filters as well. In his equations the β factor depends on λ not only indirectly by optical density (as in other authors' equations) but also directly (see eqs. (1)–(3)) in Konovalov 1992). The detailed description of methods the used during particular campaigns can be found in the papers mentioned above. Basic methodological information was gathered by Koblentz-Mishke *et al.* (1995). During the ULISSE campaign the pigment absorption measurements were carried out according to Tassan and Ferrari's method, published later in

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[1] Underwater Light Seatruth Satellite Experiment, in co-operation with the Commission of the European Union Joint Research Centre, Ispra, Italy and the Institute of Oceanology PAS.

Table 1. Specification of the input empirical data collection

Trophic type* of water	Surface chlorophyll $C_a(0)$ concentration range [$\mathrm{mg\,m^{-3}}$]	Numbers of ($a_{pl}(\lambda)$, pigments) data**		References to β-correction factors used
Oceanic (case 1 waters) data				
O–I	<0.05	20	(6)	Konovalov (1992), Koblentz-Mishke *et al.* (1995)
O–II	0.05–0.1	61	(48)	
O–III	0.1–0.2	70	(–)	
M	0.2–0.5	46	(30)	
I	0.5–1	73	(10)	
E–I	1–2	154	(28)	
Baltic and Black Sea (case 2 waters) data				
O–III	0.1–0.2	28	(8)	Konovalov (1992), Koblentz-Mishke *et al.* (1995), Tassan & Ferrari (1995)
M	0.2–0.5	109	(17)	
I	0.5–1	199	(18)	
E–I	1–2	138	(8)	
E–II	2–5	167	(54)	
E–III	5–10	159	(94)	
E–IV	10–20	148	(81)	
E–V	>20	28	(12)	

* Trophic type symbols: O – oligotrophic, M – mesotrophic, I – intermediate, E – eutrophic;

** The numbers without brackets denote all data sets with pigments determined by various methods, whereas the numbers in brackets relate to the data sets with pigments determined by HPLC.

1995, *i.e.* Readouts of spectra passed through the filter (transmission mode) and reflected by the filter (reflection mode) were produced which were repeated after the filters had been bleached with $\mathrm{Ca(ClO)_2}$. The spectra were corrected with the β factor established by Tassan and Ferrari (1995). Owing to significant differences at all stages of the procedure it was difficult to harmonise all the β factors used.

The concentration of chlorophyll a in seawater determined with standard methods (C_a = chl a + pheo) was known for all 1400 samples. Moreover, in 414 cases the concentrations of other pigments belonging to the chlorophyll and carotenoid groups were determined by HPLC: chls a, b, c, photosynthetic carotenoids, *e.g.* fucoxanthin, $19'$ but-fucoxanthin, $19'$ hex-fucoxanthin, peridinin, prasinoxanthin and α-carotene, and photoprotecting carotenoids, *e.g.* diadinoxanthin, alloxanthin, zeaxanthin, diatoxanthin, lutein, antheraxanthin and β-carotene (Paramonova 1971, Koblentz-Mishke & Semenova 1975, Semenova 1975, Kornushenko *et al.* 1980, Olaizola 1996).

Applying these data by means of the successive approximations method given in Appendix 2, the reverse problem of finding the unknowns in formulae (1)–(7) was solved. The specific absorption coefficients of particular groups of pigments are described as the sums of Gaussian bands. The product $C_I\, d$ is given as a function of the total chlorophyll concentration C_a in the seawaters examined.

As a first approximation the portion of the functional PS2 reaction centers f_c is assumed to be determined as follows (Ficek *et al.* 1999):

$$f_c\ [\log C_a(0),\, \tau] = \frac{1}{0.65}\left(1 - \frac{F_0}{F_M}\right), \tag{8a}$$

where the ratio F_0/F_M is approximated by the polynomial

$$\frac{F_0}{F_M} = \sum_{m=0}^{2}\left[\sum_{n=0}^{2} A_{m,\,n}\,(\log C_a(0))^n\right]\tau^m, \tag{8b}$$

where $\tau = K_{PAR}\, z$ – optical depth in the sea. The values of $A_{m,\,n}$ are given in Table 2. The f_c portion is shown graphically in Fig. 1.

Table 2. Values of $A_{m,\,n}$ in eq. (8b)

n \ m	0	1	2
0	0.6958	–0.08513	0.009619
1	–0.1295	0.03742	–0.005846
2	–0.09065	0.02902	–0.004215

Equations (8a) and (8b) were obtained on the basis of statistical analyses of f_c values from about 100 sites in the World Ocean (where the surface chlorophylls *a* concentration ranges from 0.022 to 4.6 mg chl $a\,\mathrm{m}^{-3}$) using active stimulated fluorescence techniques (Kolber & Falkowski 1993, Babin *et al.* 1996). The f_c portions were obtained from the relation $f_c \approx \Delta\Phi_M/0.65$ ($\Delta\Phi_M$ – the maximum change in the quantum yield of phytoplankton chlorophyll variable fluorescence, *i.e.* the ratio $(F_M - F_0)/F_M$ of variable and maximum fluorescences of phytoplankton chlorophyll measured *in vivo* in dark-adapted conditions). These generalisations show (Fig. 1) that the f_c portion is much higher in eutrophic than in oligotrophic water and varies with depth. It is usually lower near the surface and in deep water than at intermediate depths. This behaviour of the f_c portion is possible because of the joint influence of both light conditions and nutrient concentrations. At present we are unable to explain these relationships in detail.

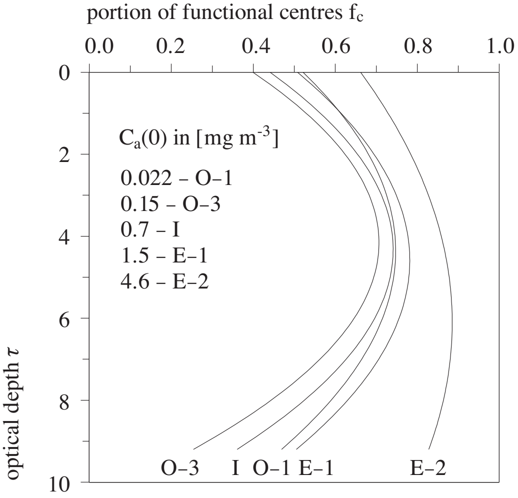

Fig. 1. Modelled vertical distributions of the fraction of the functional PS2 reaction centers f_c for various trophic types of waters

The general shape of the absorption spectra, *i.e.* the positions of their peaks and inflexion points were determined on the basis of all 1400 data sets. In further detailed analysis of the absolute values of the absorption coefficients and products $C_I\, d$, only the data sets with pigment concentrations measured by HPLC were applied.

3. Results and discussion

A summary of the results is given in Table 3 together with eqs. (9) and (10). Table 3 gives the model characteristics of the specific absorption Gaussian bands of the major groups of phytoplankton pigments. They are mean values for all types and cases of ocean waters.

The 'unpackaged' specific absorption coefficient of the j-pigments group (*i.e.* chlorophylls a, chlorophylls b, *etc.* as given in the Table) can be determined from Table 3 data by the following sum of Gaussian bands:

$$a^*_j(\lambda) = \sum_i a^*_{\mathrm{max,\,i}}\; e^{-\frac{1}{2}\left(\frac{\lambda-\lambda_{\mathrm{max},\,i}}{\sigma_i}\right)^2}, \tag{9}$$

where i – Gaussian band numbers of major groups of phytoplankton pigments (*e.g.* chlorophylls a, chlorophylls b, chlorophylls c, photosynthetic carotenoids and photo-protecting carotenoids).

A graphical illustration of these coefficients for individual pigment groups compared with data published by other authors is given in Fig. 2. The differences between the absorption capacity of different pigments determined by various authors can be caused by methodological errors as well as

Table 3. Model characteristics of the specific absorption components of Gaussian bands:

chlorophylls *a* (A–1)–(A–6)

Characteristic	Gaussian band number					
	A–1	A–2	A–3	A–4	A–5	A–6
$\lambda_{\mathrm{max},\,i}$	381	420	437	630	675	700
σ_i	33.8	8.25	6.50	89.8	8.55	101
$a^*_{\mathrm{max},\,i}$	0.0333	0.0268	0.0580	0.0005	0.0204	0.0005

chlorophylls *b* (B–1)–(B–6)

Characteristic	Gaussian band number					
	B–1	B–2	B–3	B–4	B–5	B–6
$\lambda_{\mathrm{max},\,i}$	380	442	452	470	609	655
σ_i	194	7.45	5.6	10.5	16.0	18.5
$a^*_{\mathrm{max},\,i}$	0.0059	0.0145	0.0631	0.0514	0.0083	0.0257

chlorophylls *c* (C–1)–(C–4)

Characteristic	Gaussian band number			
	C–1	C–2	C–3	C–4
$\lambda_{\mathrm{max},\,i}$	408	432	460	583
σ_i	16.1	7.93	14.2	32.2
$a^*_{\mathrm{max},\,i}$	0.0561	0.0234	0.0072	0.0133

photosynthetic (PSC–1, PSC–2) and photoprotecting (PPC–1)–(PPC–3) carotenoids

Characteristic	Gaussian band number				
	PSC–1	PSC–2	PPC–1	PPC–2	PPC–3
$\lambda_{\mathrm{max},\,i}$	490	532	451	464	493
σ_i	17.1	22.8	32.0	8.60	12.0
$a^*_{\mathrm{max},\,i}$	0.0313	0.0194	0.0632	0.0253	0.0464

where

$\lambda_{\mathrm{max},\,i}$ – centre of band [nm],
σ_i – dispersion of band [nm],
$a^*_{\mathrm{max},\,i}$ – maximum specific absorption coefficient [m^2 (mg pigment)$^{-1}$].

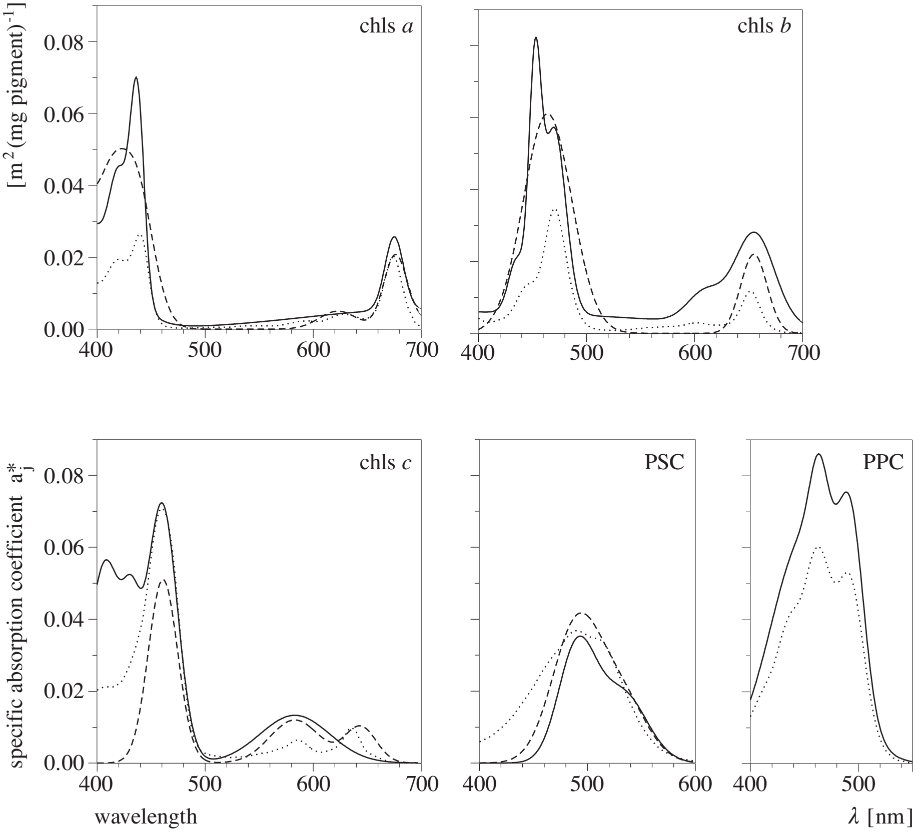

Fig. 2. ‘Unpackaged’ specific absorption spectra modelled in this paper for the major pigment groups (solid lines) and postulated by other authors: Hoepffner & Sathyendranath (1991) (dashed lines), Bidigare *et al.* (1990) (dotted lines)

by the natural diversity of absorption pigment properties under different conditions.

The total mean phytoplankton absorption spectra in solvent by specific absorption coefficients of individual pigment groups, approximated by ourselves (Table 3), are shown in Fig. 3. There is satisfactory conformity between the modelled and real spectra of absorption.

The behaviour of the product $C_I\, d$ appears to be very complicated (see the explanation in Bricaud *et al.* 1995). However, its relations with depth z or τ in the sea were found to be statistically similar to the relations of chlorophyll concentration $C_a(z)$ or $C_a(\tau)$ (Woźniak *et al.* 1992) with surface chlorophyll $C_a(0)$ (see Figs. 4a,b). From this similarity, the following formula for $C_I\, d$ was established:

$$C_I\, d = 24.65\, C_a^{0.75015}. \tag{10}$$

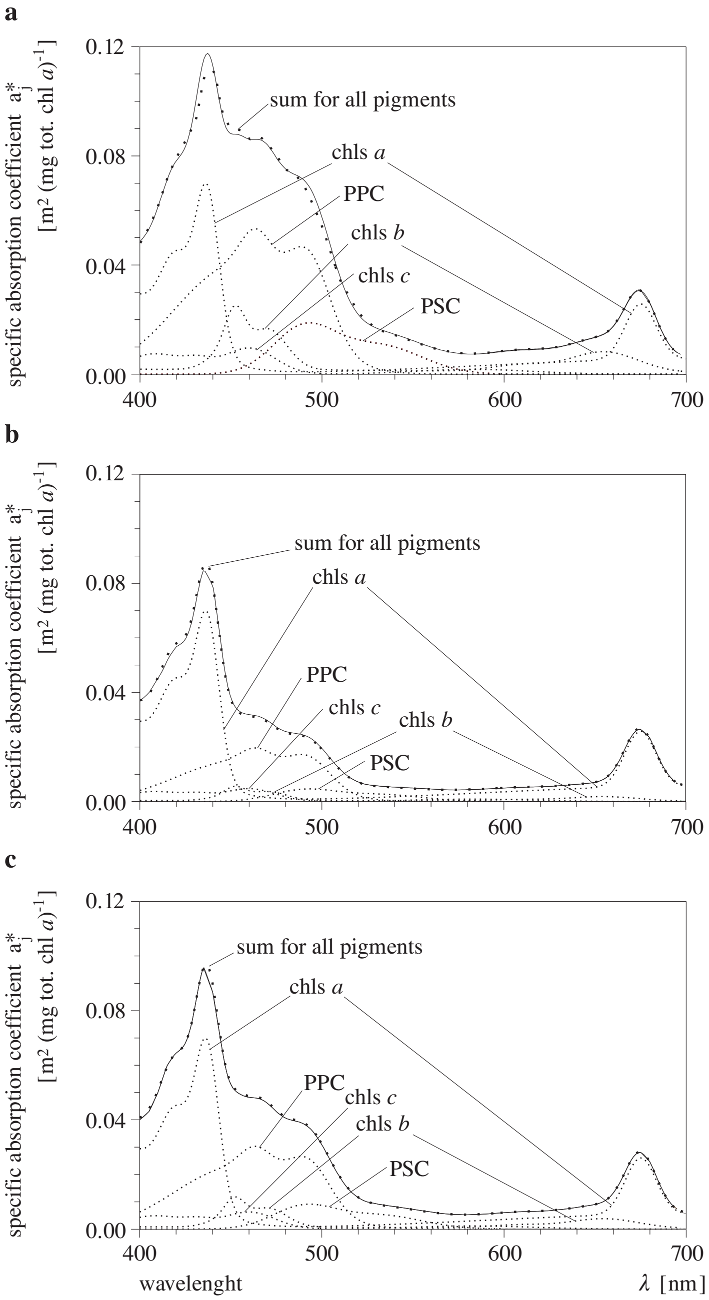

Fig. 3. Specific absorption spectra of phytoplankton pigments in solvent: the mean for groups determined (after correction for the package effect) on the basis of the measured data sets (solid lines) and modelled by the sum of the spectra of the major component pigments (dashed lines); for case 1 waters (a), for case 2 waters (b), mean for both water cases (c)

Its graphical representation is given in Fig. 4c.

Formula (10) is applied to determine $C_I\, d$ in the respective equations of the phytoplankton absorption model presented in this paper.

The models showing the dependence of C_a on depth and surface chlorophylls concentration given in Woźniak *et al.*, (1992a,b, 1995) can be applied together with formula (10) to determine the distribution of products $C_I\, d$ in various types of seas (see the examples in Figs. 4d,e,f).

Some idea of the approximation accuracy of the modelled phytoplankton absorption is given in Figs. 5a,b. The model absorption coefficient (mean for 400–700 nm)

$$\overline{a}_{pl} = \frac{1}{300}\, C_a \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} a^{*}_{pl}\,(\lambda)\, d\lambda, \tag{11}$$

determined on the basis of given pigment concentrations (for the same 414 phytoplankton samples as were used to work out the model) is compared to the measured data of absorption. A similar comparison of our measured data with those estimated by means of the Bricaud *et al.* (1995) model is given in Figs. 5c,d to illustrate the differences.

Both comparisons are shown together to show the extent to which the statistical estimation errors of phytoplankton absorption differ in the following two cases: (i) if, in the model, the absorption properties are assumed to depend on chlorophyll a concentration only (Bricaud *et al.* 1995 model), and (ii) if we additionally take the diversity of accessory pigment optical properties into consideration (this model).

Table 4 gives the calculated errors in both modelled estimations.

As one can see, the accuracy of the models is satisfactory in both cases. The respective statistical errors are less than 50%, the value of which can be regarded as a typical error in the measurement of chlorophyll a concentration and the estimation of its absorption coefficient a_{pl} (see 'Discussion' in Bricaud *et al.* 1995). However, the statistical error of the model presented in this paper appears to be much smaller than that of the model published by Bricaud *et al.* (1995). This is because the diversified composition of photosynthetic pigments caused by photo- and chromatic acclimation processes have been taken into account, whereas the model by Bricaud *et al.* (1995) considers only the changes in chlorophyll a concentration. Fig. 6 shows the errors in estimating the spectral

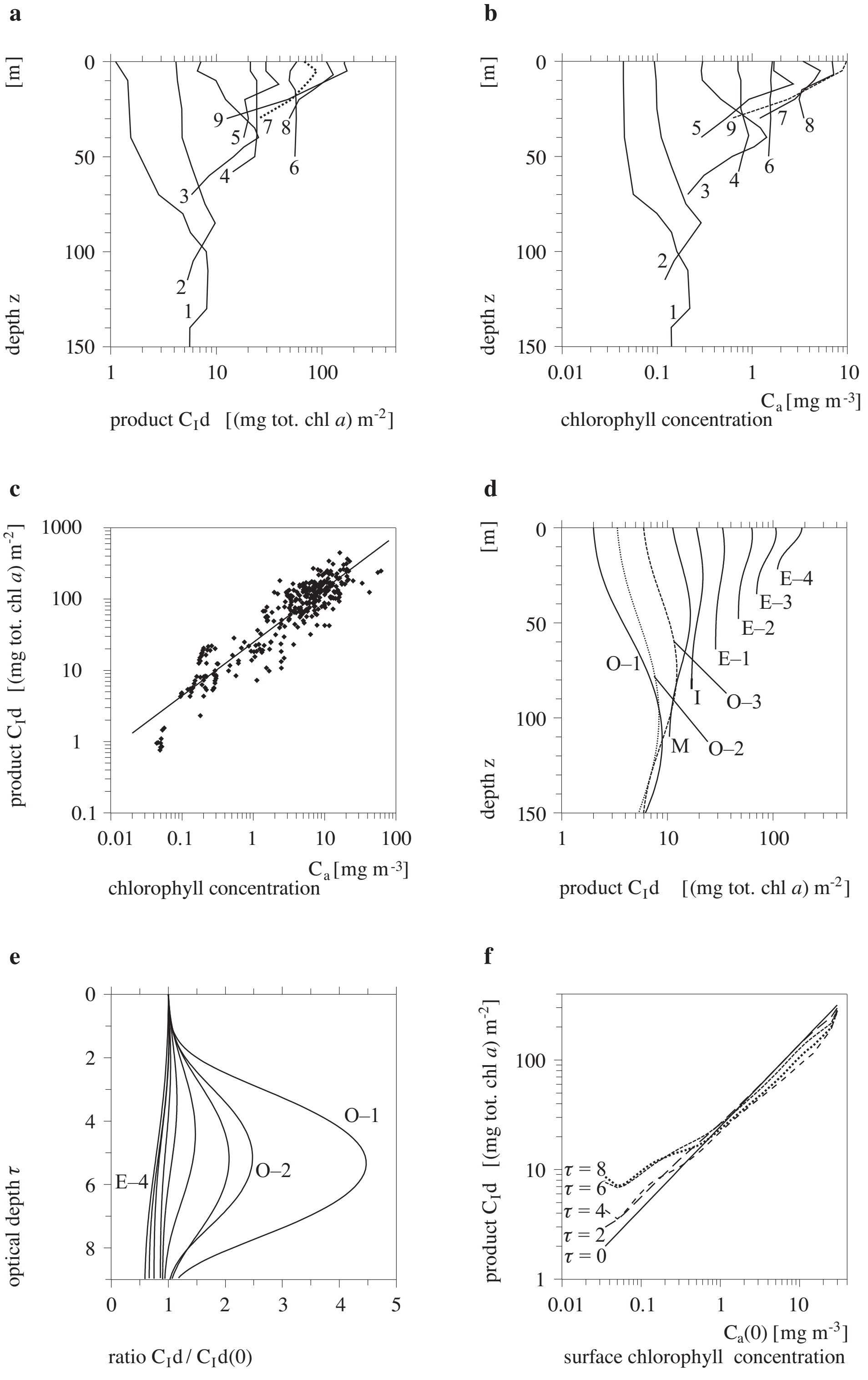
a
depth z [m]
0
50
100
150
1
10
100
product $C_I d$ [(mg tot. chl *a*) m^{-2}]
1
2
3
4
5
6
7
8
9
b
depth z [m]
0
50
100
150
0.01
0.1
1
10
C_a [mg m^{-3}]
chlorophyll concentration
1
2
3
4
5
6
7
8
9
c
product $C_I d$ [(mg tot. chl *a*) m^{-2}]
1000
100
10
1
0.1
0.01
0.1
1
10
100
C_a [mg m^{-3}]
chlorophyll concentration
d
depth z [m]
0
50
100
150
1
10
100
product $C_I d$ [(mg tot. chl *a*) m^{-2}]
E–4
E–3
E–2
E–1
O–1
I
O–3
M
O–2
e
optical depth τ
0
2
4
6
8
0
1
2
3
4
5
ratio $C_I d / C_I d(0)$
O–1
O–2
E–4
f
product $C_I d$ [(mg tot. chl *a*) m^{-2}]
100
10
1
0.01
0.1
1
10
$C_a(0)$ [mg m^{-3}]
surface chlorophyll concentration
τ = 8
τ = 6
τ = 4
τ = 2
τ = 0

Fig.4. Relations of the product $C_I\, d$ with the total chlorophyll a concentration C_a and depth in the sea. Examples of $C_I\, d$ vertical profiles: 1–3 Atlantic, 4–9 Baltic (a); examples of C_a concentration profiles for the same stations as in Fig. 4a (b); relationship between the product $C_I\, d$ and concentration C_a: observed (points) and approximated by formula (10) (line) (c); modelled vertical profiles of $C_I\, d$ in various trophic types of stratified case 1 waters (curves O1–E4 correspond to various water trophicities given in Table 1) (d) and (e); modelled dependence of $C_I\, d$ on surface chlorophyll concentration $C_a(0)$ for various optical depths τ in stratified case 1 waters (f). In Figs. d–f the $C_a[C_a(0),\, z]$ model from Woźniak *et al.* (1992a,b) was applied

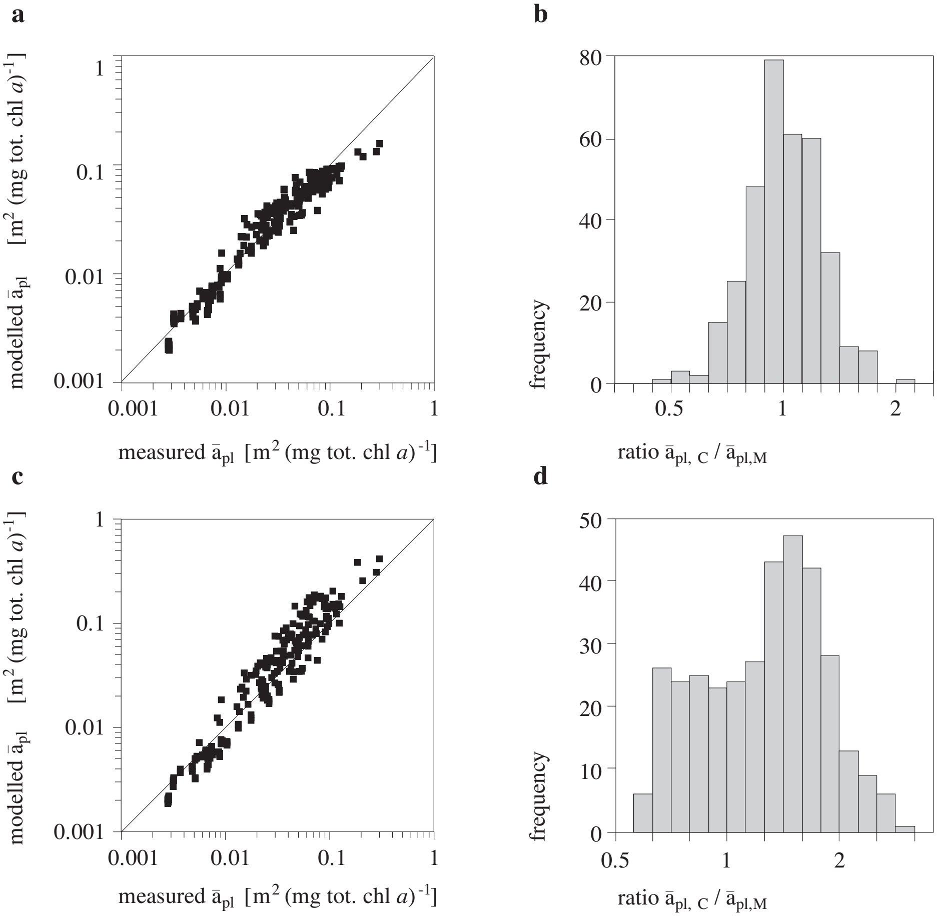

Fig. 5. Comparison between modelled $(\overline{a}_{pl,\,C})$ and measured $(\overline{a}_{pl,\,M})$ phytoplankton absorption coefficients and error histograms at various stations and depths in the sea: for the model presented in this paper (a) and (b); for the model in Bricaud *et al.* (1995) (c) and (d)

Table 4. The relative errors in the mean phytoplankton absorption coefficient (in the 400–700 nm range) at different depths in the oceans estimated from the models

	Arithmetic statistics		Logarithmic statistics			
	systematic	statistical	systematic	range of variability		variability factor
	$\langle\varepsilon\rangle$ [%]	σ_ε [%]	$\langle\varepsilon\rangle_g$ [%]	σ_- [%]	σ_+ [%]	x
present model	+3.86	± 23.7	+0.69	–19.2	+26.3	1.25
Bricaud *et al.* 1995	+32.7	± 48.1	+24.1	–14.4	+80.0	1.45

where

$\overline{a}_{pl,\,M}$ – measured phytoplankton absorption coefficient;

$\overline{a}_{pl,\,C}$ – modelled phytoplankton absorption coefficient;

$\varepsilon = \frac{\overline{a}_{pl,\,C}-\overline{a}_{pl,\,M}}{\overline{a}_{pl,\,M}}$ – error;

$\langle\varepsilon\rangle$ – arithmetic mean of errors;

σ_ε – standard deviation of errors (statistical error);

$\langle\varepsilon\rangle_g = 10^{[\langle\log(\overline{a}_{pl,\,C}/\overline{a}_{pl,\,M})\rangle]} - 1$ – geometric mean of errors;

$\sigma_- = 10^{[\langle\log(\overline{a}_{pl,\,C}/\overline{a}_{pl,\,M})\rangle-\sigma_{\log}]} - 1$ and $\sigma_+ = 10^{[\langle\log(\overline{a}_{pl,\,C}/\overline{a}_{pl,\,M})\rangle+\sigma_{\log}]} - 1$;

$x = 10^{\sigma_{\log}}$ – variability factor;

$\langle\log(\overline{a}_{pl,\,C}/\overline{a}_{pl,\,M})\rangle$ – arithmetic mean of $\log(\overline{a}_{pl,\,C}/\overline{a}_{pl,\,M})$;

$\sigma_{\log}$ – standard deviation of $\log(\overline{a}_{pl,\,C}/\overline{a}_{pl,\,M})$.

absorption coefficients $a_{pl}(\lambda)$ calculated using the present model. They are somewhat larger than those for mean absorption. Except for the long-wave range ($\lambda \approx 700\,\mathrm{nm}$), they do not exceed 30%. The present model is therefore a good enough reflection of the spectral structure of $a_{pl}(\lambda)$. The comparison between the estimated and measured $a_{pl}(\lambda)$ spectra most often resembles the examples given in Fig. 7.

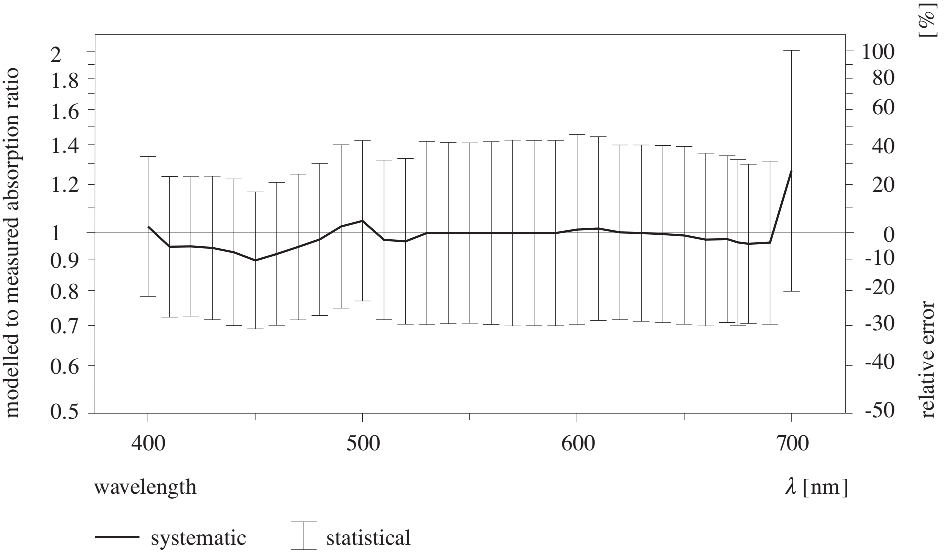

Fig. 6. Spectra of the errors of estimating the light absorption coefficients determined from the model presented

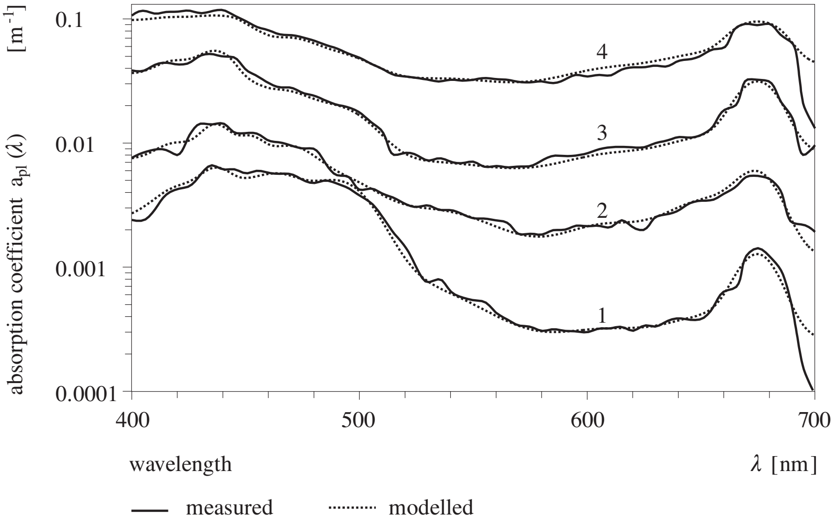

Fig. 7. Typical examples of comparison of the phytoplankton light absorption coefficient spectra $a_{pl}(\lambda)$ measured in various seas (solid lines) and calculated from the model (dashed lines) for different pigment concentrations in mg m^{-3}: 1 – $C_a = 0.047$, $C_b = 0.006$, $C_c = 0.007$, $C_{PSC} = 0.021$, $C_{PPC} = 0.062$ (surface water of the Atlantic); 2 – $C_a = 0.19$, $C_b = 0.097$, $C_c = 0.041$, $C_{PSC} = 0.103$, $C_{PPC} = 0.015$ (deep water of the Black Sea); 3 – $C_a = 1.6$, $C_b = 0.16$, $C_c = 0.081$, $C_{PSC} = 0.17$, $C_{PPC} = 0.19$ (surface water of the Baltic); 4 – $C_a = 10.1$, $C_b = 0.97$, $C_c = 0.22$, $C_{PSC} = 0.91$, $C_{PPC} = 0.33$ (deep water of the Baltic)

4. Conclusions

The model equations (1) to (10), together with Tables 2 and 3, allow the total phytoplankton spectral absorption coefficient $a^*_{pl}(\lambda)$ as well as all the component absorption coefficients defined by formulae (1) to (4) to be estimated. The concentrations of individual groups of pigments, optical depth in the sea and measured concentrations of chlorophylls a are the input data for these estimations. It is especially important to distinguish the portions of light absorbed by photoprotecting (non-photosynthetic) pigments, photosynthetic pigments and also photosynthetic pigments at the functional reaction centres only. This possibility enables us to consider the effects of acclimation and is important for determining the true quantum yield of phytoplankton photosynthesis (Dera 1995, Ficek 1999).

The model estimation of $C_I\,d$ is, of course, a preliminary one, but it is the first one to give a general view of its dependence on environmental conditions (Fig. 4).

The model can be improved by introducing more accurate empirical input data, and also by including other pigments such as phycobilins, which have been not considered in this paper.

References

Allali K., Bricaud A., Claustre H., 1997, *Spatial variations in the chlorophyll-specific absorption coefficients of phytoplankton and photosynthetically active pigments in the equatorial Pacific*, J. Geophys. Res., 102, 12413–12423.

Babin M., Morel A., Claustre H., Bricaud A., Kolber Z., Falkowski P. G., 1996, *Nitrogen- and irradiance-dependent variations of the maximum quantum yield of carbon fixation in eutrophic, mesotrophic and oligotrophic marine systems*, Deep-Sea Res., 43, 1241–1272.

Bidigare R., Ondrusek M. E., Morrow J. H., Kiefer D. A., 1990, *In vivo absorption properties of algal pigments*, Ocean Optics 10, Proc. SPIE, 1302, 290–302.

Bricaud A., Babin M., Morel A., Claustre H., 1995, *Variability in the chlorophyll-specific absorption coefficients of natural phytoplankton: analysis and parameterisation*, J. Geophys. Res., 100, 13321–13332.

Dera J., 1995, *Underwater irradiance as a factor affecting primary production*, Diss. and monogr., Inst. Oceanol. PAS, 7, 110 pp.

Ficek D., 1999, *Modelling of quantum yield of photosynthesis in various marine systems*, Ph.D. thesis, Inst. Oceanol. PAN, (in Polish).

Ficek D., Kuzio M., Ostrowska M., *Spatial distribution of phytoplankton photosynthesis activity in different trophic types of sea*, (in Polish), (in press).

Hoepffner N., Sathyendranath S., 1991, *Effect of pigment composition on absorption properties of phytoplankton*, Mar. Ecol. Progr. Ser., 73 (1), 11–23.

Hulst van de, 1981, *Light scattering by small particles*, Dover Publ. Inc., New York, 470 pp.

Kaczmarek S., Ferrari G. M., 1996, *Phytoplankton pigments absorption spectra*, M. C. Ooms (ed.), (op. cit.), 421–472.

Koblentz-Mishke O. I., Semenova M. A., 1975, *Phytoplankton pigments of mesotrophic and eutrophic regions of the tropical Pacific, works of IO RAN 102*, Nauka, Moskva, 131–139, (in Russian).

Koblentz-Mishke O. I., Woźniak B., Ochakovskiy Yu. E. (eds.), 1985, *Utilisation of solar energy in the photosynthesis of the Baltic and Black Sea phytoplankton*, Izd. Inst. Okeanol. AN SSSR, Moskva, 336 pp., (in Russian).

Koblentz-Mishke O. I., Belayeva G. A. (eds.), 1987, *The ecosystems of the Baltic Sea in May–June 1984*, Izd. Inst. Okeanol. AN SSSR, 439 pp., (in Russian).

Koblentz-Mishke O. I., Woźniak B., Kaczmarek S., Konovalov B. V., 1995, *Assimilation of light energy by marine phytoplankton. Part 1. Light absorption capacity of the Baltic and Black Sea phytoplankton*, Oceanologia, 37 (2), 145–169.

Kolber Z., Falkowski P. G., 1993, *Use of active fluorescence to estimate phytoplankton photosynthesis in situ*, Limnol. Oceanogr., 38 (8), 1646–1665.

Konovalov B. V., Belayeva G. A., Bekasova O. D., Kosakowska A., 1990, *Light-absorbing capacity of phytoplankton in the Gulf of Gdańsk in May 1987*, Oceanologia, 28, 25–38.

Konovalov B. V., 1992, *Determination of light absorption coefficient by seston components using absorption spectrum on the membrane filter*, Okeanologiya, 32, 588–593, (in Russian).

Kornushenko G. A., Vedernikov V. I., Koblentz-Mischke O. I., Konovalov B. V., 1980, *Results of thin-layer chromatography application for determination of carotenoids in Black sea phytoplankton*, [in:] M. E. Vinogradov (ed.), (op. cit.), 127–131.

Majchrowski R., 1999, *Influence of irradiance on the marine phytoplankton light absorption characteristics*, Ph.D. thesis, Inst. Oceanol. PAN, (in Polish).

Morel A., Bricaud A., 1981, *Theoretical results concerning light absorption in a discrete medium and application to specific absorption of phytoplankton*, Deep-Sea Res., 28, 1375–1393.

Morel A., Antoine D., Babin M., Dandonneau Y., 1996., *Measured and modeled primary production in the northeast Atlantic (Eumeli JGOFS program): the impact of natural variations in photosynthetic parameters on model predictive skill*, Deep-Sea Res., 43, 1273–1304.

Olaizola M., 1996, *High performance liquid chromatography*, [in:] M. C. Ooms (ed.), (op. cit.), 363–382.

Ooms M. C. (ed.), 1996, *ULISSE (Underwater Light Seatruth Satellite Experiment) Data Catalogue*, Commiss. Europ. Union Joint Res. Centre, Ispra, Italy, Spec. publ., 1.96.29, 506 pp.

Paramonova L. I., 1971, *Experience of the use of the thin-layer chromatography technique to divide phytoplankton pigments aboard ship*, [in:] M. E. Vinogradov (ed.), (op. cit.), 88–91.

Semenova M. A., 1975, *Investigation of marine phytoplankton carotenoids*, Ph.D. thesis, IB RAN, Leningrad, (in Russian).

Tassan S., Ferrari G. M., 1995, *An alternative approach to absorption measurements of aquatic particles retained on filters*, Limnol. Oceanogr., 40 (8), 1347–1357.

Vinogradov M. E., (ed.), 1971, *Functioning of pelagic communities in the tropical regions of the ocean – materials of 44th cruise of r/v 'Vityaz'*, Nauka, Moskva, 271 pp., (in Russian).

Vinogradov M. E., (ed.), 1980, *Pelagic ecosystems in the Black Sea*, Nauka, Moskva, 250 pp., (in Russian).

Woźniak B., 1991, *International ecological seminar. Application of physical methods (satellite and fluorescence) to studies of marine ecosystem (October 10–12, 1990, Sopot, Poland)*, Oceanologia, 30, 141–142.

Woźniak B., Ostrowska M., 1990, *Optical absorption properties of phytoplankton in various seas*, Oceanologia, 29, 91–115.

Woźniak B., Dera J., Koblentz-Mishke O. I., 1992a, *Modelling the relationship between primary production, optical properties, and nutrients in the sea*, Ocean Optics 11, Proc. SPIE, 1750, 246–275.

Woźniak B., Dera J., Koblentz-Mishke O. I., 1992b, *Bio-optical relationships for estimating primary production in the Ocean*, Oceanologia, 33, 5–38.

Woźniak B., Dera J., Semovski S., Hapter R., Ostrowska M., Kaczmarek S., 1995, *Algorithm for estimating primary production in the Baltic by remote sensing*, Stud. i Mater. Oceanol., 68, 91–123.

Woźniak B., Dera J., Majchrowski R., Ficek D., Koblentz-Mishke O. I., Darecki M., 1997, *IO PAS initial model of marine primary production for remote sensing application*, Oceanologia, 39 (4), 397–395.

Appendix 1

Notation

Symbol	Significance	Units
a	light absorption coefficient:	m^{-1}
a_{pl}	– of phytoplankton	m^{-1}
$a_{pl,\,C}$	– of phytoplankton calculated (modelled)	m^{-1}
$a_{pl,\,M}$	– of phytoplankton measured	m^{-1}
a^*	specific absorption coefficient	
a^*_{pl}	– of phytoplankton	m^2 (mg tot. chl $a)^{-1}$
$a^*_{pl,\,S}$	– of phytoplankton pigments in solvent	m^2 (mg tot. chl $a)^{-1}$
a^*_a	– of chlorophylls a in solvent	m^2 (mg tot. chl $a)^{-1}$
a^*_b	– of chlorophylls b in solvent	m^2 (mg chl $b)^{-1}$
a^*_c	– of chlorophylls c in solvent	m^2 (mg chl $c)^{-1}$
a^*_{PSC}	– of photosynthetic carotenoids in solvent	m^2 (mg $PSC)^{-1}$
a^*_{PPC}	– of photoprotecting carotenoids in solvent	m^2 (mg $PPC)^{-1}$
a^*_{PSP}	– of photosynthetic pigments	m^2 (mg tot. chl $a)^{-1}$
$a^*_{PSP,\,f_c}$	– of part of photosynthetic pigments connected with functional reaction centres PS2,	m^2 (mg tot. chl $a)^{-1}$
$a^*_{PPP,\,S}$	– of photoprotecting pigments in solvent	m^2 (mg tot. chl $a)^{-1}$
a^*_{PPP}	– of photoprotecting pigments	m^2 (mg tot. chl $a)^{-1}$
$a^*_{\mathrm{max,\,i}}$	specific absorption coefficient at the maximum of the i-th Gaussian band	m^2 (mg pigment$)^{-1}$
a^*_j	specific absorption coefficient of the j-th pigment group	m^2 (mg pigment$)^{-1}$
C_a	sum of chlorophylls a + pheo, or total chlorophyll (chl a + divinyl chl a) concentrations	mg tot. chl a m^{-3}
$C_a(0)$ $C_a(z)$ or $C_a(\tau)$	sum of chlorophylls a + pheo, or total chlorophyll (chl a + divinyl chl a) concentrations in the surface water, at depth z or optical depth τ	mg tot. chl a m^{-3}
C_b, C_c, C_{PPC}, C_{PSC}	concentrations of chl b, chl c, photoprotecting carotenoids, photosynthetic carotenoids	mg pigment m^{-3}
C_I	intercellular chlorophylls a concentration	mg tot. chl a m^{-3}

Notation (continued)

Symbol	Significance	Units
d	cell diameter	m
f_c	portion of functional PS2 reaction centres	dimensionless
HPLC	High Performance Liquid Chromatography	
K_{PAR}	PAR irradiance attenuation coefficient	m^{-1}
PAR	photosynthetically available radiation	
PSP	photosynthetic pigments	
PPP	non-photosynthetic (photoprotecting) pigments	
PSC	photosynthetic carotenoids	
PPC	photoprotecting carotenoids	
PS2	photosystem 2	
O	oligotrophic type of water	
M	mesotrophic type of water	
I	intermediate type of water	
E	eutrophic type of water	
Q	efficiency factor for absorption	dimensionless
Q^*	package effect function	dimensionless
z	depth in the sea	m
β	pathlength amplification correction factor	dimensionless
λ	wavelength of the light	nm
$\lambda_{\mathrm{max,\,i}}$	centre of Gaussian band	nm
ρ'	optical parameter of cell	dimensionless
τ	optical depth in the sea	dimensionless
σ_i	dispersion of Gaussian band	nm

Appendix 2

Outline of the successive approximation method

Aims of the computation:

- to calculate model parameters of the Gaussian specific absorption bands of the major groups of phytoplankton pigments;
- to find values of the product $C_I\, d$ for the 414 phytoplankton samples examined.

To achieve these aims, an algorithm consisting of several numerical programs was constructed. This algorithm can be classified as the successive approximations method.

The 414 sets of the following quantities was used as input data to the algorithm:

- $a^*_{pl,\,l}(\lambda)$ – measured phytoplankton absorption spectra,
- $C_{a,\,l}$, $C_{b,\,l}$, $C_{c,\,l}$, $C_{PSC,\,l}$, $C_{PPC,\,l}$ – concentration of the main phytoplankton pigment groups.

The ordinal indices used in this appendix are as follows:
$l = 1 \ldots 414$ – index of the sample number,
k – iteration index,
j – pigment group index (*i.e.* chls a, chls b, chls c, PPC, PSC),
i – Gaussian band number.

The general pattern of individual (k) iteration is as follows:

step 1: the computation of the spectral functions of the package effect separately for each analysed spectrum $a^*_{pl,\,l}(\lambda)$ from the equations:

$$^{(k)}Q^*_l\,(\lambda) = \begin{cases} a^*_{pl,l}(\lambda)/^{(k-1)}a^*_{pl,\,S,\,l}(\lambda) & \text{for} \quad a^*_{pl,\,l} \le {}^{(k-1)}a^*_{pl,\,S,\,l} \\ 1 & \text{for} \quad a^*_{pl,\,l} > {}^{(k-1)}a^*_{pl,\,S,\,l} \end{cases}$$

where $^{(k-1)}a^*_{pl,\,S,\,l}(\lambda)$ is determined from the equations (on the basis of $(k-1)$ iterated results):

$$\begin{aligned} a^*_{pl,\,S,\,l}(\lambda) &= \frac{1}{C_{a,\,l}}\Big[C_{a,\,l}\, a^*_a(\lambda) + C_{PSC,\,l}\, a^*_{PSC}(\lambda) + \\ &+ \quad C_{b,\,l}\, a^*_b(\lambda) + C_{c,\,l}\, a^*_c(\lambda) + C_{PPC,\,l}\, a^*_{PPC}(\lambda)\Big], \end{aligned}$$

(the index S denotes absorption in solvent)

$$a^*_j(\lambda) = \sum_i a^*_{\max,\,i}\, e^{-\frac{1}{2}\left(\frac{\lambda-\lambda_{\max,\,i}}{\sigma_i}\right)^2}.$$

In these computations the known values of $a^*_{pl,S,l}(\lambda)$, $C_{a,l}$, $C_{b,l}$, $C_{c,l}$, $C_{PSC,l}$, $C_{PPC,l}$, which are input data, and the parameters of the Gaussian specific absorption bands found in the previous iteration $(k-1)$ are used. For the first iteration, the parameters of the specific absorption bands were taken according to Hoepffner & Sathendranath (1991).

step 2: calculation of the set of phytoplankton cell spectral optical parameters for all analysed spectra from the equation:

$$^{(k)}\rho'_l(\lambda) = f^{-1}\left[{}^{(k)}Q^*_l(\lambda)\right],$$

where f^{-1} is the inverse function to $Q^* = f(\rho')$ (eq. (5)). The function f^{-1} was established by numerical polynomial approximation:

$$\begin{aligned}\rho' &= 0.054612 - 4.83185\,(\log_{10} Q^*) + 9.31228\,(\log_{10} Q^*)^2 + \\ &+ 8.92935\,(\log_{10} Q^*)^3 + 9.58374\,(\log_{10} Q^*)^4,\end{aligned}$$

step 3: calculation of the set of $C_I\,d$ values (taken for various wavelengths measured as a pseudo-spectral function), which result from the spectra $^{(k)}\rho'_l(\lambda)$, using the dependence

$$^{(k)}C_I\,d_l(\lambda) = \frac{^{(k)}\rho'_l(\lambda)}{^{(k-1)}a^*_{pl,S,l}(\lambda)},$$

step 4: determination of the set of substitute values of $\langle C_l\,d\rangle_l$ for all samples, by averaging the pseudo-spectral functions $C_I\,d_l(\lambda)$ with the weights of the spectral light absorption coefficients by phytoplankton:

$$^{(k)}\langle C_I\,d\rangle_l = \frac{\int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} {}^{(k)}C_I\,d_l(\lambda)\,a^*_{pl,l}(\lambda)\,d\lambda}{\int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} a^*_{pl,l}(\lambda)d\lambda},$$

step 5: calculation of the set of maximal cell specific absorption coefficients (in the so-called 'black body' state) from the relation:

$$^{(k)}a^*_{\mathrm{maximal,l}} = \frac{3}{2\ {}^{(k)}\langle C_I\,d\rangle_l},$$

step 6: calculation of the set of correcting spectral cell absorption efficiency factors:

$$^{(k)}Q_l^{\mathrm{correcting}}(\lambda) = \begin{cases} a^*_{pl,l}(\lambda)/{}^{(k)}a^*_{\mathrm{maximal},l} & \text{for} \quad a^*_{pl,l} \le {}^{(k)}a^*_{\mathrm{maximal},l} \\ 1 & \text{for} \quad a^*_{pl,l} > {}^{(k)}a^*_{\mathrm{maximal},l} \end{cases}$$

step 7: calculation of the set of corrected spectra of the package effect functions:

$$^{(k)}Q_l^{*\,\mathrm{correcting}}(\lambda) = f\left[{}^{(k)}Q_l(\lambda)\right],$$

where the function $Q^* = f(Q)$ becomes

$$\begin{aligned} Q^* = 1 - \Big(&0.00118189 - 1.27698\,\log_{10}(1-Q) - 0.933118\,(\log_{10}(1-Q))^2 + \\ &- 0.463738\,(\log_{10}(1-Q))^3 - 0.144978\,(\log_{10}(1-Q))^4 + \\ &- 0.0248388\,(\log_{10}(1-Q))^5 - 0.00175777\,(\log_{10}(1-Q))^6\Big), \end{aligned}$$

after numerical reduction of parameter ρ' from the set of equations describing the package effect function (eq. 5) and the efficiency factor for absorption (van de Hulst 1981), which is given below:

$$Q = 1 + \frac{2\exp(-\rho')}{\rho'} + 2\,\frac{2\exp(-\rho') - 1}{\rho'^2},$$

step 8: determination of the set of correcting spectral specific absorption coefficients of phytoplankton pigments in solvent:

$$^{(k)}a^*_{pl,\,S,\,l}(\lambda) = a^*_{pl,\,l}(\lambda)/{}^{(k)}Q_l^{*\,\mathrm{correcting}}(\lambda),$$

step 9: determination of the mean spectral specific pigments absorption coefficient for all sets of samples analysed:

$$^{(k)}\overline{a^*_{pl,\,S}}(\lambda) = \frac{1}{N}\sum_{l=1}^{N} {}^{(k)}a^*_{pl,\,S,\,l}(\lambda),$$

where N = number of sample.

step 10: Gaussian analysis of the spectrum $^{(k)}\overline{a^*_{pl,\,S}}(\lambda)$ and finding the model characteristics of the specific absorption for n Gaussian bands:

- $\lambda_{\mathrm{max},\,i}$ – centre of band,
- $a'_{\mathrm{max},\,i}$ – $[\mathrm{m}^2(\mathrm{mg\,tot.\,chl}\ a)^{-1}]$ – specific absorption coefficients in the band maximum,
- σ_i – dispersion of band,

where i = 1, 2,... n.

Approximate wavelengths of these band maxima $\lambda_{\mathrm{max},\,i}$ are initially established on the basis of all experimental spectra $a^*_{pl}(\lambda)$, with the use of differential spectroscopy and analysis of the 4th derivative maximum position of absorption spectra. According our practice, satisfactory results of estimation can be achieved by decomposition spectra of $a_{pl}(\lambda)$ on about

21 individual absorption bands ($n = 21$).
The complete set of n Gaussian band parameters $({}^{(k)}\lambda_{\max,\,i},\ {}^{(k)}a'_{\max,\,i},\ {}^{(k)}\sigma_i)$ for the mean spectrum ${}^{(k)}\overline{a^*_{pl,\,S}}(\lambda)$ can be calculated using the non-linear regression algorithm from the 'Statistica' programme, modified by ourselves.

step 11: assignment of individual bands to the various major groups of pigments. This was achieved by analysing the correlation coefficients between pigment group concentrations and band fields

$$P_i = \int\limits_{400\text{nm}}^{700\text{nm}} a'_{\max,\,i}\, e^{-\frac{1}{2}\left(\frac{\lambda-\lambda_{\max,\,i}}{\sigma_k}\right)^2} d\lambda,$$

for all spectra ${}^{(k)}a^*_{pl,\,S,\,l}(\lambda)$.
Particular bands were attached to the pigment groups for which the correlation coefficients were largest.

step 12: appropriate maximum values for individual absorption bands are calculated as

$$(a^*_{\max,\,i})_j = a'_{\max,\,i}/(\overline{C_j/C_a}),$$

where $(\overline{C_j/C_a})$ – mean for all sample ratios of the j-pigment concentration group to chlorophyll a concentration.

The calculations were completed at the 5th iteration, after which the results were similar to those from the 4th iteration.