Model of the *in vivo* spectral absorption of algal pigments. Part 2. Practical applications of the model*

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Abstract

The article describes applications and accuracy analyses of a statistical model of light absorption by phytoplankton that accounts for the influence of photo- and chromatic acclimation on its absorption properties. Part 1 of this work (see Woźniak *et al.* 2000, this volume) describes the mathematical apparatus of the model. Earlier models by Woźniak & Ostrowska (1990) and by Bricaud *et al.* (1995, 1998) are

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analysed for comparison. Empirical verification of these three models shows that the new model provides a much better approximation of phytoplankton absorption properties than do the earlier models. The statistical errors in estimating the mean absorption coefficient $\overline{a}_{pl}$, for example, are $\sigma_{+} = 36\%$ for the new model, whereas for the earlier models the figures are $\sigma_{+} = 43\%$ (Bricaud *et al.* 1995, 1998) and $\sigma_{+} = 59\%$ (Woźniak & Ostrowska 1990). Example applications are given of the new model illustrating the variability in phytoplankton absorption properties with depth and trophicity of the sea.

1. Introduction

Part 1 of our presentation of the new statistical model of light absorption by phytoplankton (Woźniak *et al.* 2000 in this volume) contained a description of the mathematical apparatus of the model. In Part 2 we shall demonstrate the model's practical utility and its accuracy. To this end, the following results and examples of its application are given:

- results of a comparison of the estimated and measured phytoplankton light absorption coefficients as a means of verifying the model,
- examples of the model's application in describing the variability of the absorption properties of the natural phytoplankton population *in situ*.

The errors arising out of the use of this model are compared with those of the respective statistical models worked out earlier by Woźniak & Ostrowska (1990) and Bricaud *et al.* (1995, 1998).

2. Verification results

The following empirical data were used to determine the errors in the model:

- $E_d(\lambda, z)$ – spectra of underwater downward irradiances at different depths measured by Woźniak & Montwiłł (1973), Woźniak *et al.* (1983),
- $a_{pl}(\lambda, z)$ – spectra of phytoplankton absorption coefficients determined according to the method in Koblentz-Mishke *et al.* (1995),
- $C_a(z)$ – chlorophyll a concentrations determined spectrophotometrically according to Strickland & Parsons (1968).

Samples for determining $C_a(z)$ and $a_{pl}(\lambda, z)$ were taken at the same depths as those where the spectra of underwater downward irradiances $E_d(\lambda, z)$ were measured.

528 sets of data from the Atlantic Ocean, Baltic Sea and Black Sea were analysed. The data from the Baltic (235 sets) were obtained during

the Polish-Italian ULISSE experiment (see Ooms 1996, Olaizola 1996), those from elsewhere (293 sets) during Polish-Russian cruises (see *e.g.* Koblentz-Mishke *et al.* 1985, Woźniak *et al.* 1997 and the papers cited therein, Polish-Russian database, unpublished).

Applying these values of $E_d(\lambda, z)$ and $C_a(z)$, functions of spectral fitting $< F_j(z) >_{\Delta z=60}$ for photosynthetic pigments and the Potentially Destructive Radiation $< PDR^*(z) >_{\Delta z=60}$ at various depths in the sea were determined in accordance with the algorithm presented in Part 1 of this paper (ibid. Table 1, pp. 182–188). With the aid of these functions, the concentrations of particular groups of pigments were then calculated: chlorophyll b – C_b, chlorophyll c – C_c, photosynthetic carotenoids – C_{PSC} and photoprotecting carotenoids – C_{PPC}, from which the phytoplankton *in vivo* absorption coefficients $a_{pl,\,C}(\lambda)$ were finally computed. The model was verified by comparing the measured $a_{pl,\,M}(\lambda)$ and calculated $a_{pl,\,C}(\lambda)$ absorption coefficients. Some results of this comparison are presented in Fig. 1 for the mean phytoplankton absorption coefficient in the 400–700 nm spectral range. This coefficient is defined as follows:

$$\bar{a}_{pl} = \frac{1}{300} \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} a_{pl}(\lambda)\, d\lambda. \tag{1}$$

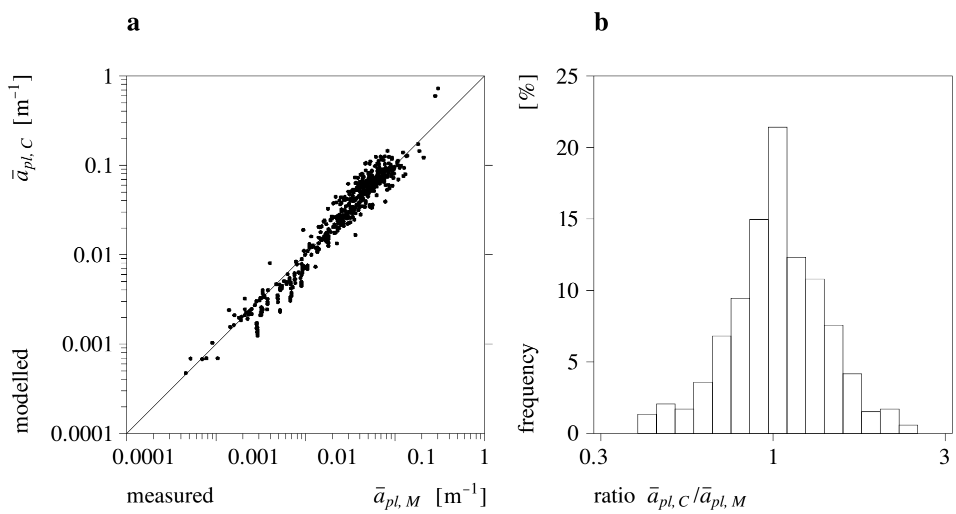

Fig. 1. Comparison of modelled and measured mean phytoplankton absorption coefficients (a) and frequency distribution of the ratio $\bar{a}_{pl,\,C}/\bar{a}_{pl,\,M}$ (b); at various stations and depths in the sea – determined with the new model

The variability of these coefficients ranges over four orders of magnitude and, as the graph shows, the measured and calculated values overlap. Errors of estimation are given in Table 1 (case a). The error histogram on a logarithmic scale (the ratio of measured to calculated mean absorption coefficients) is also given on the graph. Clearly, these errors are relatively small compared to the usual empirical error: for example, the systematic logarithmic error is 2.5% and the statistical error σ_+ is about 36%. The result thus seems to be satisfactory.

Table 1. Results of verification of absorption models: a – errors of our new model, b – errors of the Bricaud *et al.* (1995, 1998) model, c – errors of the Woźniak & Ostrowska (1990) model

	Arithmetic statistics		Logarithmic statistics			
	systematic	statistical	systematic	standard error factor	statistical	
	$\langle\varepsilon\rangle$ [%]	σ_ε [%]	$\langle\varepsilon\rangle_{\mathrm{g}}$ [%]	x	σ_- [%]	σ_+ [%]
a	7.42	± 33.3	2.49	1.36	–26.5	36
b	24.5	± 47.4	16.6	1.43	–30.1	43
c	112	± 105	90.6	1.59	–37	59

where

$\varepsilon = (\bar{a}_{pl,\,C} - \bar{a}_{pl,\,M})/\bar{a}_{pl,\,M}$ – errors,

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

σ_ε – standard deviation of errors (statistical error),

$\langle\varepsilon\rangle_{\mathrm{g}} = 10^{[\langle\log(\bar{a}_{pl,\,C}/\bar{a}_{pl,\,M})\rangle]} - 1$ – logarithmic mean of errors,

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

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

$x = 10^{\sigma_{\log}}$ – standard error factor,

$\sigma_- = \frac{1}{x} - 1$ and
$\sigma_+ = x - 1$.

The two earlier models (Bricaud *et al.* 1995, 1998, Woźniak & Ostrowska 1990; see eqs. (1) and (2) in Part 1 of this paper, pp. 178, 179) were also verified using the same empirical data sets. The results of those verifications are presented in Figs. 2 and 3, and Table 1 (cases b and c). The table shows that the systematic error of the model by Bricaud *et al.* (1995) is 16.6%, the statistical error (σ_+) 43%. These percentages are higher than those of our new model. The errors in the Woźniak & Ostrowska (1990) model are even greater, the systematic one being *ca* 91% and the statistical (σ_+) one *ca* 59%.

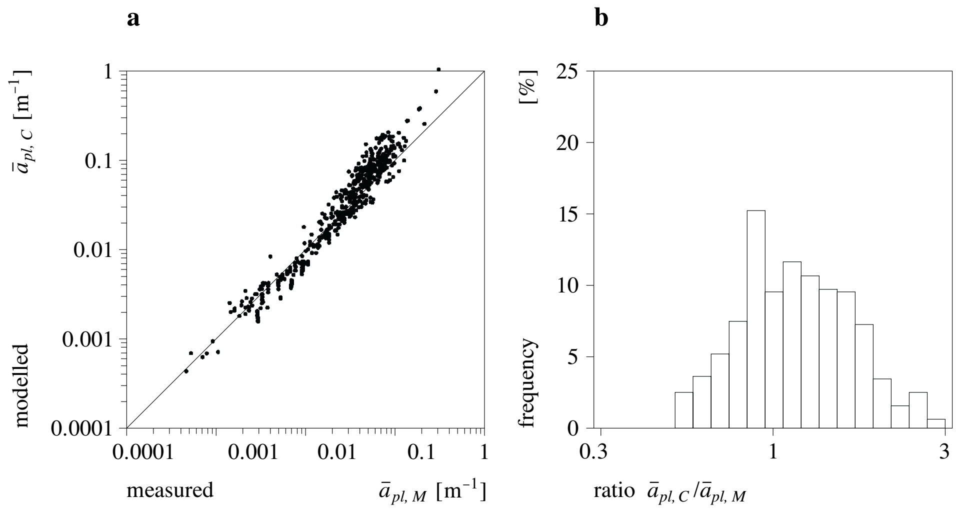

Fig. 2. Comparison of modelled and measured mean phytoplankton absorption coefficients (a) and frequency distribution of the ratio $\bar{a}_{pl,C}/\bar{a}_{pl,M}$ (b); at various stations and depths in the sea – determined with the model by Bricaud *et al.* (1995, 1998)

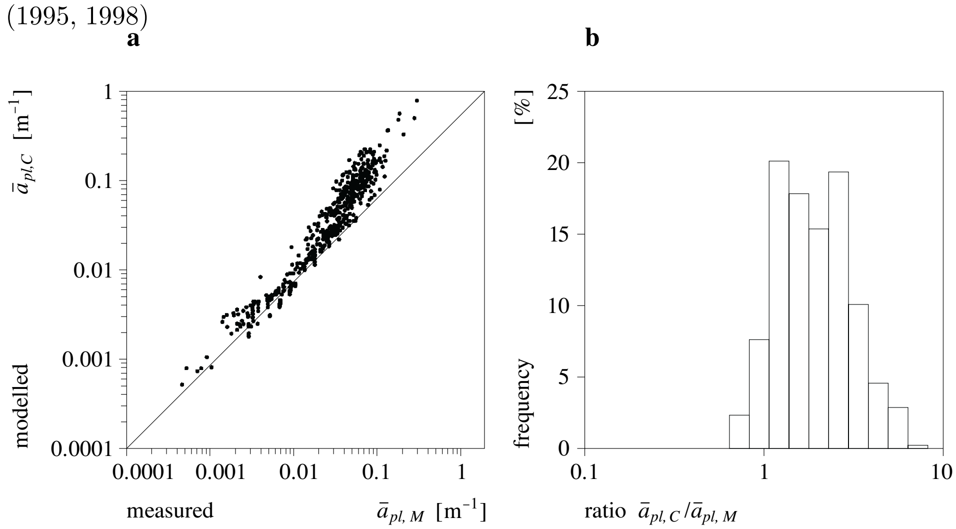

Fig. 3. Comparison of modelled and measured mean phytoplankton absorption coefficients (a) and frequency distribution of the ratio $\bar{a}_{pl,C}/\bar{a}_{pl,M}$ (b); at various stations and depths in the sea – determined with the model by Woźniak & Ostrowska (1990)

Figure 4 compares these measured phytoplankton absorption spectra and the respective absorption spectra determined with these three models. The coefficients calculated with our new model fit the experimental data best.

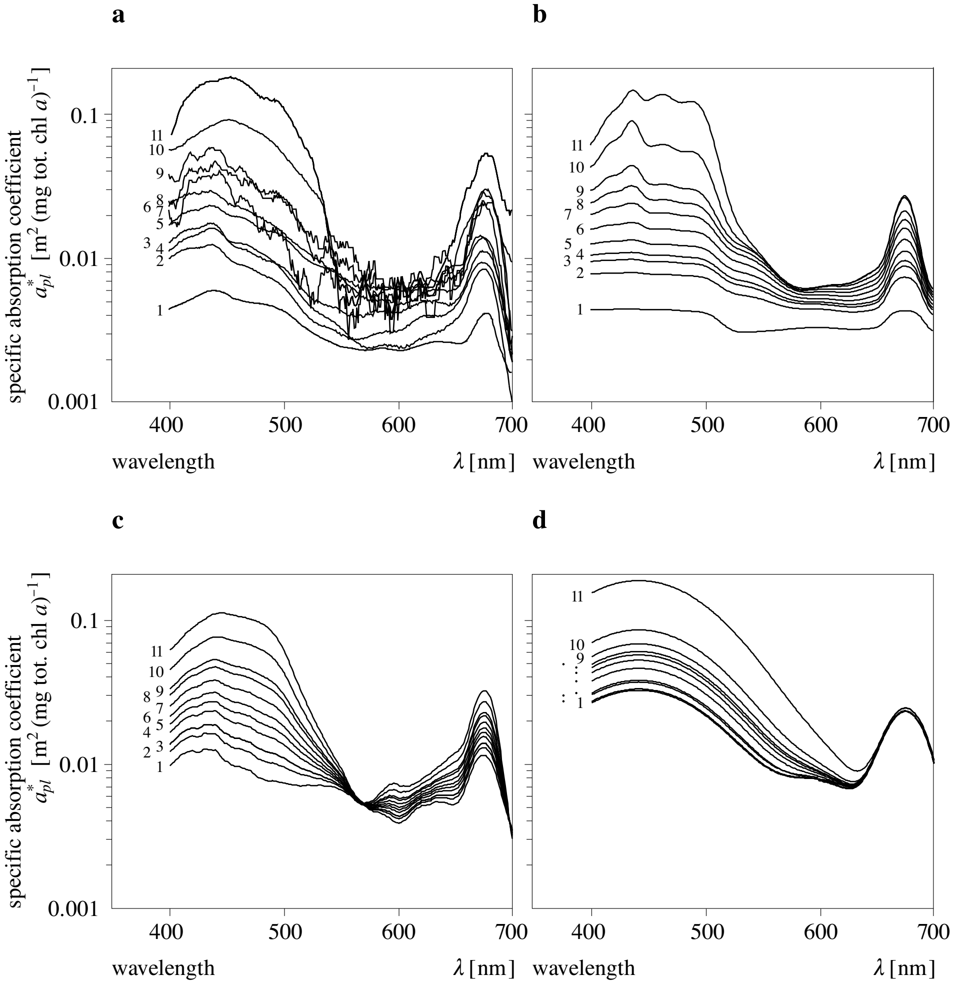

Fig. 4. Comparison of phytoplankton spectral specific absorption coefficients: measured *in situ* (a); determined with our new model (b); determined with the model by Bricaud *et al.* (1995, 1998) (c); determined with the model by Woźniak & Ostrowska (1990) (d). The numbers allotted to the spectra indicate the following trophic types of seawater: 1 – $C_a(0) = 156$ mg tot. chl a m^{-3}; 2 – $C_a(0) = 33.2$ mg tot. chl a m^{-3}; 3 – $C_a(0) = 11.4$ mg tot. chl a m^{-3}; 4 – $C_a(0) = 7.4$ mg tot. chl a m^{-3}; 5 – $C_a(0) = 3.2$ mg tot. chl a m^{-3}; 6 – $C_a(0) = 1.15$ mg tot. chl a m^{-3}; 7 – $C_a(0) = 0.61$ mg tot. chl a m^{-3}; 8 – $C_a(0) = 0.30$ mg tot. chl a m^{-3}; 9 – $C_a(0) = 0.24$ mg tot. chl a m^{-3}; 10 – $C_a(0) = 0.14$ mg tot. chl a m^{-3}; 11 – $C_a(0) = 0.047$ mg tot. chl a m^{-3}, and the sources of the respective empirical data: 1 – Lake Fukami-ike, Japan (Takematsu *et al.*, 1981); 2–5 – Baltic Sea 1994 – ULISSE experiment (Ooms 1996); 6–8 – Baltic Sea 1990 – results of the voyage of r/v 'Professor Shtockman' (Koblentz-Mishke *et al.* 1985); 9, 11 – Atlantic 1973 – results of the voyage of r/v 'Mendeleyev'(Polish-Russian database, unpublished); 10 – Pacific (Kishino *et al.*, 1986)

3. Applications of the new model

This section describes applications of the new model. The calculated vertical profiles of the mean specific absorption coefficients of phytoplankton $\overline{a}^*_{pl}$ (the total for all pigments) determined for surface irradiance $PAR_0(0^+) = 695$ μEin m^{-2} s^{-1} and that of the photosynthetic pigment component $\overline{a}^*_{pl,\,PSP}$ only are shown in Fig. 5. The mean values of these coefficients for various trophic types of waters were determined from the following relationships:

$$\overline{a}^*_{pl} = \frac{1}{300} \int\limits_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} a^*_{pl}(\lambda)\, d\lambda, \tag{2}$$

$$\overline{a}^*_{pl,\,PSP} = \frac{1}{300} \int\limits_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} a^*_{pl,\,PSP}(\lambda)\, d\lambda. \tag{3}$$

For photosynthetic pigments $\overline{a}^*_{pl,\,PSP}$ (Fig. 5b), the mean specific absorption coefficient increases with depth. This increase seems to be caused by rising concentrations of accessory photosynthetic pigments (the reader is reminded that the coefficient is computed per unit mass of chlorophyll a; see also Figs. 8b, c and d in Majchrowski & Ostrowska 2000, this volume, p. 172). In the case of the total mean specific phytoplankton absorption coefficient (for all pigments) $\overline{a}^*_{pl}$, there is a minimum at a certain depth in the vertical profile (Fig. 5a). This minimum moves towards the sea surface when there is an increase in the trophicity of the water. Above the minimum, the mean specific absorption coefficient $\overline{a}^*_{pl}$ increases as the concentration of photoprotecting carotenoids does so. Below the minimum, the increase in the mean specific absorption coefficient $\overline{a}^*_{pl}$ is due to a rise in the relative concentrations of accessory photosynthetic pigments. The earlier two models were unable to explain this effect; our new model seems to enable us to do so.

Figure 6 shows spectra of the phytoplankton specific absorption coefficient (total $a^*_{pl}(\lambda)$) determined for surface irradiance $PAR_0\,(0^+) = 1400$ μEin m^{-2} s^{-1} and different optical depths (from $\tau = 0$ as far as the double euphotic zone, $\tau = 9.2$) in mesotrophic waters. The spectra peak near the sea surface, but then decrease with depth within the euphotic zone, ($\tau = 4.6$); below this, however, they increase with depth. The behaviour of the spectral coefficient $a^*_{pl}(\lambda)$ at different depths follows the $\overline{a}^*_{pl}$ vertical profiles presented above.

Figure 7 presents one more application of the new model. This shows spectra of the phytoplankton specific absorption coefficient $a^*_{pl}(\lambda)$ in

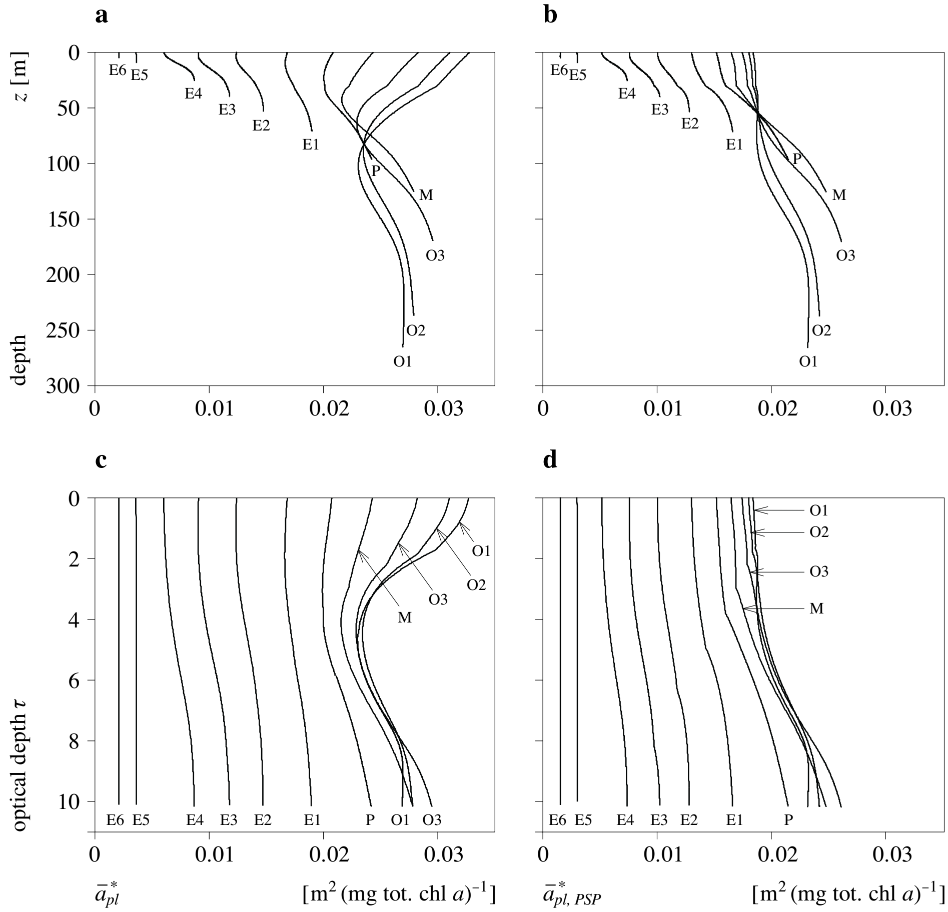

Fig. 5. Modelled depth profiles of mean specific absorption coefficients for: total phytoplankton pigments $\overline{a}^*_{pl}$ (a and c), photosynthetic pigments $\overline{a}^*_{pl,\,PSP}$ (b and d); determined for surface irradiance $PAR_0(0^+) = 695$ μEin m^{-2} s^{-1} and different trophic types of water, where: O1 – $C_a(0) = 0.035$ mg tot. chl a m^{-3}; O2 – $C_a(0) = 0.07$ mg tot. chl a m^{-3}; O3 – $C_a(0) = 0.15$ mg tot. chl a m^{-3}; M – $C_a(0) = 0.35$ mg tot. chl a m^{-3}; P – $C_a(0) = 0.7$ mg tot. chl a m^{-3}; E1 – $C_a(0) = 1.5$ mg tot. chl a m^{-3}; E2 – $C_a(0) = 3.5$ mg tot. chl a m^{-3}; E3 – $C_a(0) = 7$ mg tot. chl a m^{-3}; E4 – $C_a(0) = 15$ mg tot. chl a m^{-3}; E5 – $C_a(0) = 35$ mg tot. chl a m^{-3}; E6 – $C_a(0) = 70$ mg tot. chl a m^{-3}

oligotrophic, intermediate and eutrophic waters, all for an optical depth $\tau = 1$, but with a different irradiance $PAR_0\,(0^+)$ at the sea surface. A higher irradiance level at the surface is known to raise the Potentially Destructive Radiation energy PDR^* which, in turn, elevates the concentration of photoprotecting pigments. As can be seen from this figure, the highest

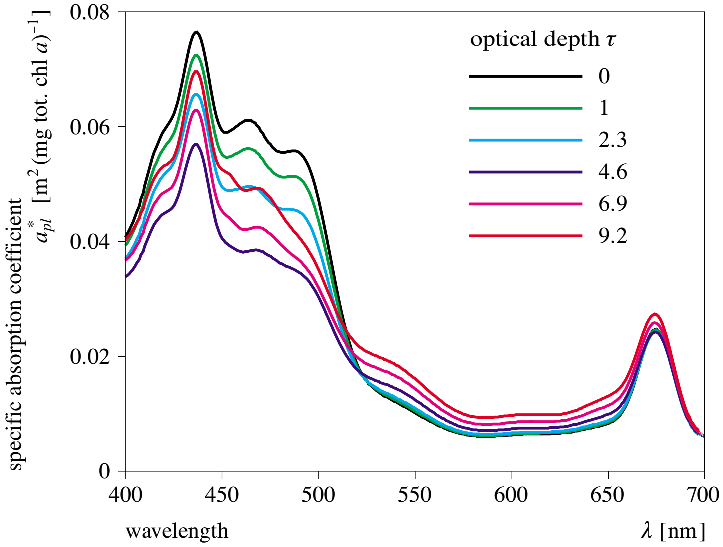

Fig. 6. Examples of specific phytoplankton absorption spectra determined with our new model for different optical depths (calculations were carried out for a surface irradiance $PAR_0(0^+) = 1400\ \mu\text{Ein m}^{-2}\text{ s}^{-1}$ and a surface chlorophyll concentration $C_a(0) = 0.35$ mg tot. chl a m^{-3})

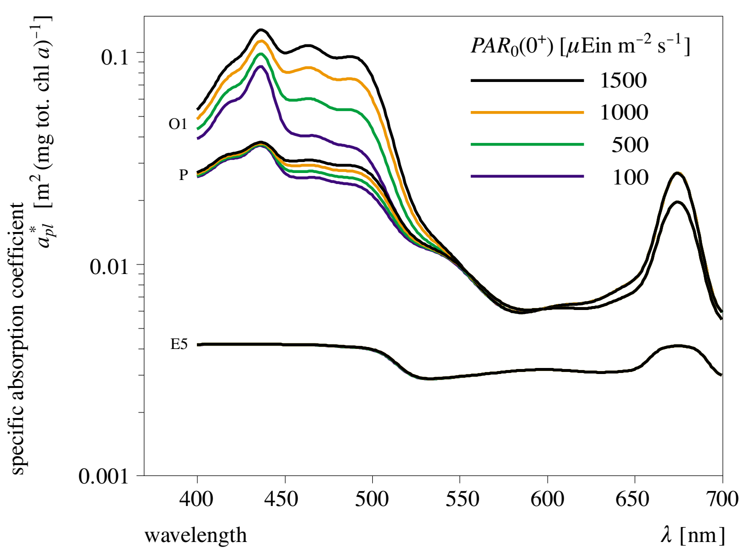

Fig. 7. Examples of specific absorption coefficient spectra for oligotrophic (O1 – $C_a(0) = 0.035$ mg tot. chl a m^{-3}), intermediate (P – $C_a(0) = 0.7$ mg tot. chl a m^{-3}) and eutrophic (E5 – $C_a(0) = 35$ mg tot. chl a m^{-3}) waters, and different surface irradiances. The calculations were carried out for an optical depth $\tau = 1$

value of the specific phytoplankton absorption coefficient was recorded when the irradiance reached a maximum. The total coefficients $a^*_{pl}(\lambda)$ decrease as the surface irradiance does so. In the theoretical extreme case when $PAR_0\,(0^+) \approx 0$, the level of $a^*_{pl}(\lambda)$ drops to the level of $a^*_{pl,\,PSP}(\lambda)$, which implies the absence of photoprotecting pigments in the phytoplankton cells. It is characteristic that phytoplankton specific absorption coefficients are highest in oligotrophic waters, in which case these coefficients alter significantly with variations in the irradiance level. In eutrophic waters the $a^*_{pl}(\lambda)$ coefficients and their reaction to the irradiance level are less pronounced. The earlier models by Bricaud *et al.* (1995, 1998) and Woźniak & Ostrowska (1990) do not take this effect into account.

4. Final remarks and conclusions

The statistical model of *in vivo* light absorption by phytoplankton pigments presented in Part 1 (Woźniak *et al.* 2000, this volume) and Part 2 of this paper is a nontrivial one. Physically well argued, it accounts for the ability of the photosynthetic apparatus of the phytoplankton cells to adapt to external conditions (photoacclimation, chromatic acclimation and the package effect), mainly to the spectrum of the ambient underwater irradiance. Moreover, unlike the previous single-component models, the new model is a multi-component one, accounting as it does for the influence on absorption of both chlorophyll *a* and the other photosynthetic and photoprotecting groups of pigments (chlorophyll *b*, chlorophyll *c*, photosynthetic carotenoids and photoprotecting carotenoids).

Because of inherent difficulties with measurement, the model does not cover the influence of phycobilins on the total light absorption by natural populations of marine phytoplankton. But as these components are rarely present in marine phytoplankton, this influence seems to be weak (Parsons *et al.* 1977). The empirical verification of the model demonstrates that errors in estimating the absorption coefficients are relatively small compared to the usual empirical error (the statistical error is about 36%). Furthermore, comparison of this model with the earlier single-component models by Bricaud *et al.* (1995) (statistical error 43%) and by Woźniak & Ostrowska (1990) (statistical error 59%) shows a significant improvement in the estimation of pigment absorption. This suggest that the modification of the earlier models has been useful.

The new statistical model is a synthesis of our knowledge of phytoplankton absorption properties in various trophic types of waters and at different depths in the sea. Fig. 5 illustrates these properties with an example of the mean specific light absorption coefficients of the photosynthetic pigments $\overline{a}^{\,*}_{pl,\,PSP}$ (in the visible spectral range) and the vertical profiles of all the pigments $\overline{a}^*_{pl}$ in different water types. It can be seen from the graph that the range of variability of the coefficients is almost 20 fold. The specific absorption generally falls when the water trophicity index C_a increases, and the characteristic changes in the coefficients with depth in the sea are evident. The specific absorption coefficient of photosynthetic pigments $\overline{a}^*_{pl,\,PSP}$ increases with depth as the concentration of accessory photosynthetic pigments does so. In contrast, the total specific absorption coefficient of the phytoplankton $\overline{a}^*_{pl}$ reaches a minimum at a certain depth. Above this, the specific absorption increases, because the relative concentration of photoprotecting pigments does so. Below the depth of minimum specific absorption the total absorption $\overline{a}^*_{pl}$ is practically equal to the absorption of photosynthetic pigments $\overline{a}^*_{pl,\,PSP}$, which increases with depth for the reasons mentioned above.

The present model may have a wide practical application in ecological modelling, in remote monitoring of the sea and for other purposes. Example applications of the model in the fluorometric study of phytoplankton are described by Ostrowska *et al.* (2000a and b), and its application in an investigation of the photosynthesis quantum yield in the paper by Ficek *et al.* (2000), this volume.

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