Remote sensing of vertical phytoplankton pigment distributions in the Baltic: new mathematical expressions. Part 3: Non-photosynthetic pigment absorption factor*

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Abstract

This paper, part 3 of the description of vertical pigment distributions in the Baltic Sea, discusses the mathematical expression enabling the vertical distributions of the non-photosynthetic pigment absorption factor f_a to be estimated. The factor f_a is

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directly related to concentrations of the several groups of phytoplankton pigments and describes quantitatively the ratio of the light energy absorbed at given depths by photosynthetic pigments to the light energy absorbed by all the phytoplankton pigments together (photosynthetic and photoprotecting). Knowledge of this factor is highly desirable in the construction of state-of-the-art 'light-photosynthesis' models for remote-sensing purposes.

The expression enables f_a to be estimated with considerable precision on the basis of two surface parameters (available from satellite observations): the total chlorophyll *a* concentration at the surface $C_a(0)$ and the spectral downward irradiance $E_d(\lambda, 0)$ just below the sea surface. The expression is applicable to Baltic waters from the surface down to an optical depth of $\tau \approx 5$.

The verification of the model description of f_a was based on 400 quasi-empirical values of this factor which were calculated on the basis of empirical values of the following parameters measured at the same depths: $E_d(\lambda, z)$ (or also $PAR(z)$), $a_{pl}(\lambda, z)$, and the concentrations of all the groups of phytoplankton pigments $C_a(z)$ and $C_j(z)$ (where j denotes in turn chl *b*, chl *c*, *PSC*, *phyc*, *PPC*). The verification shows that the errors in the values of the non-photosynthetic pigment absorption factor f_a estimated using the model developed in this work are small: in practice they do not exceed 4%.

Besides the mathematical description of the vertical distribution of f_a, this paper also discusses the range of variation of its values measured in the Baltic and its dependence on the trophic index of a basin and depth in the sea. In addition, the similarities and differences in the behaviour of f_a in Baltic and oceanic basins are compared.

1. Introduction

This paper is the last in a series of three, whose objective has been to find mathematical formulas to describe the vertical distributions of phytoplankton pigments in the Baltic Sea. These formulas have been adapted for application in remote-sensing algorithms for monitoring the Baltic ecosystem. The two previous articles in this series (Ostrowska et al. 2007 and Majchrowski et al. 2007, both in this volume) give mathematical formulas approximating the vertical distributions of total chlorophyll *a* and the concentrations of the other phytoplankton accessory pigments (photosynthetic PSP[1] and photoprotecting PPP) in the Baltic. They enable the concentrations of these pigments $C_j(z)$ to be estimated at different depths in the sea from known surface total chlorophyll *a* concentrations $C_a(0)$ and known surface irradiance conditions (the spectral downward irradiance $E_d(\lambda, 0)$), both magnitudes that can be estimated by remote-sensing techniques (see, e.g., Ruddick et al. 2000, Krężel 2001, Sathyendranath et al. 2001, Darecki et al. 2003). The present paper discusses

[1]The meanings of the abbreviations and symbols used here will be found in Annex in Ostrowska et al. (2007), this volume.

the mathematical description of the vertical distributions in the Baltic of the non-photosynthetic pigment absorption factor $f_a(z)$, which is strictly related to the vertical distributions of photosynthetic and photoprotecting pigments in marine phytoplankton. This factor is crucial to the development of 'light-photosynthesis' models, particularly to the modelling of the quantum yield of photosynthesis (see Ficek et al. 2000, Woźniak et al. 2007, this volume). Its significance will be explained below.

Under natural conditions in the sea, phytoplankton produces not only chlorophyll *a*, but also various types of accessory photosynthetic and photoprotecting pigments that absorb solar energy. By absorbing part of the light reaching the phytoplankton cell, the photoprotecting carotenoids (PPC) protect chlorophyll *a* from photo-oxidation (Bidigare et al. 1990, Woźniak et al. 2007, this volume). The energy absorbed by photoprotecting pigments is not used for photosynthesis. That is why photoprotecting pigments (PPP) are often referred to as non-photosynthetic pigments (Bidigare et al. 1990, Babin et al. 1996a,b). For photosynthesis, only the energy absorbed by the photosynthetic pigments (PSP), i.e., by chlorophylls *a*, *b*, *c*, photosynthetic carotenoids (PSC) and phycobilins, is consumed. The relations between the part of the energy absorbed by phytoplankton cells that can be used in photosynthesis and the total energy absorbed by these cells are described by the above-mentioned dimensionless factor f_a. It is the ratio[2] of the solar energy absorbed at a given depth by the photosynthetic pigments in phytoplankton, the so-called photosynthetically usable radiation ($PUR_{PSP}(z)$), to the amount of that energy absorbed by all the phytoplankton pigments together ($PUR(z)$), that is, the sum of the energy absorbed by the photosynthetic pigments $PUR_{PSP}(z)$ and by the photoprotecting pigments $PUR_{PPP}(z)$:

$$f_a(z) = PUR_{PSP}(z)/PUR(z) = PUR_{PSP}(z)/(PUR_{PSP}(z) + \\ + PUR_{PPP}(z)). \qquad (1)$$

The upshot is that f_a is determined by the mutual relationship between the concentrations of photosynthetic C_{PSP} and photoprotecting pigments C_{PPP} and can theoretically take values from 0 to 1 ($f_a = 0$ if no PSP are present in the phytoplankton, i.e., when $C_{PSP} = 0$, so $PUR_{PSP} = 0$; $f_a = 1$ if no PPP are present in the phytoplankton, i.e., when $C_{PPP} = 0$, so $PUR_{PPP} = 0$).

[2]An alternative, equivalent definition of f_a would be the ratio of the variously understood quantum yields of photosynthesis: $f_a = \Phi/\Phi_{tr}$, i.e., the measured quantum yield of photosynthesis Φ, referred to quanta absorbed by all photoprotecting and photosynthetic phytoplankton pigments, to the true quantum yield Φ_{tr}, referred only to the quanta absorbed by the photosynthetic pigments.

In our earlier studies on oceanic Case 1 waters (for details, see Ficek et al. 2000), it was found that f_a usually takes values from 0.32 to 1, depending on the trophic index of the waters in question, the depth in the sea, and the irradiance conditions. An analytical description of these profiles of $f_a(\tau)$ was compiled as a function of three variables: the trophic index of the basin[3], $C_a(0)$, the optical depth in the sea τ, and the daily mean scalar irradiance just below the sea surface $PAR_0(0)$ (see eqs. (8), (9) and (10), and Tables 1, 2 and 3 in Ficek et al. 2000). Figure 1a (see p. 520, this paper) shows a plot illustrating model depth profiles of $f_a(\tau)$ in Case 1 waters of different trophic indices (calculated for the mean daily irradiance in the temperate zone $PAR(0)$= 695 μEin m^{-2} s^{-1}): in Case 1 waters f_a rises with trophic index, its value being the smallest in oligotrophic and the highest in eutrophic waters. At the same time f_a usually rises in value with increasing depth in the sea. This observation can be explained as follows: the number of high-energy radiation quanta from the short-wave end of the visible spectrum, i.e., capable of photo-oxidising chlorophyll, decreases with depth; hence, phytoplankton cells need smaller and smaller quantities of photoprotecting carotenoids (PPC) to protect them from this high-energy radiation, and PPC production declines accordingly. That is why the relative content of PPC produced by phytoplankton decreases with increasing depth. Consequently, f_a increases with both depth and the trophic index of the waters. In extreme cases, for example, in supereutrophic waters like class E5, the pigments present even at quite shallow depths are mostly photosynthetic ones, and f_a takes values close to 1. For the case illustrated in Figure 1a, f_a varies from 0.5 to 1. This was the result obtained for the mean irradiance conditions typical of the temperate zone. On the other hand, with the extremely high daily irradiances characteristic of equatorial regions, e.g., $PAR(0)$= 1300 μEin m^{-2} s^{-1}, the minimum value of f_a is about 0.32.

In the initial phase of the search for an expression to describe the vertical distributions of this non-photosynthetic pigment factor $f_a(z)$ in Baltic waters, the utility of the earlier oceanic model (Ficek et al. 2000) was assessed. The results were not encouraging. Therefore, new model formulas

[3]According to the convention adopted by our team (see, e.g., Table 6.1 in Woźniak & Dera (2007)), the trophic index (trophicity) is defined by the surface concentration of chlorophyll a $C_a(0)$. Depending on the concentration $C_a(0)$ [mg tot. chl a m^{-3}], we can distinguish the following trophic types: oligotrophic: O1 – $C_a(0) = 0.02$–0.05 (mean 0.035); O2 $C_a(0) = 0.05$–0.10 (0.075); O3 $C_a(0) = 0.10$–0.20 (0.15); mesotrophic: M $C_a(0) = 0.2$–0.5 (0.35); intermediate: I $C_a(0) = 0.5$–1.0 (0.75); eutrophic: E1 $C_a(0) = 1$–2 (1.5); E2 $C_a(0) = 2$–5 (3.5); E3 $C_a(0) = 5$–10 (7.5); E4 $C_a(0) = 10$–20 (15); E5 $C_a(0) = 20$–50 (35); E6 $C_a(0) = 50$–100 (70).

of this kind had to be developed specially for the Baltic by way of the mathematical modelling procedures and calculations presented below.

2. Analysis and modelling scheme

The following well-known relations between the quantities of energy absorbed (PUR and PUR_{PSP}) on the one hand, and the spectral distributions of the downward irradiance $E_d(\lambda)$ (or the scalar irradiance $E_0(\lambda)$) and the absorption spectra of photosynthetic pigments only $a_{pl,\,PSP}(\lambda)$ on the other were substituted in eq. (1):

$$PUR = \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} E_0(\lambda) a_{pl}(\lambda) d\lambda \approx 1.2 \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} E_d(\lambda) a_{pl}(\lambda) d\lambda, \tag{2}$$

$$PUR_{PSP} = \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} E_0(\lambda) a_{pl,\,PSP}(\lambda) d\lambda \approx 1.2 \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} E_d(\lambda) a_{pl,\,PSP}(\lambda) d\lambda. \tag{3}$$

Then, by applying the relationships $a^*_{pl} = a_{pl}/C_a$ and $a^*_{pl,\,PSP} = a_{pl,\,PSP}/C_a$, the following expression is obtained for the factor f_a at an optical depth in the sea τ:

$$f_a(\tau) = \frac{\widetilde{a}^*_{pl,\,PSP}(\tau)}{\widetilde{a}^*_{pl}(\tau)}, \tag{4}$$

where

$\widetilde{a}^*_{pl}$, $\widetilde{a}^*_{pl,\,PSP}$ – the respective mean specific absorption coefficients of chlorophyll a weighted by the irradiance spectrum in the 400–700 nm range for all phytoplankton pigments and for photosynthetic phytoplankton pigments only:

$$\widetilde{a}^*_{pl} = \frac{1}{PAR_0} \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} E_0(\lambda) a^*_{pl}(\lambda) d\lambda \approx \frac{1}{PAR} \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} E_d(\lambda) a^*_{pl}(\lambda) d\lambda, \tag{5}$$

$$\widetilde{a}^*_{pl,\,PSP} = \frac{1}{PAR_0} \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} E_0(\lambda) a^*_{pl,\,PSP}(\lambda) d\lambda \approx$$

$$\approx \frac{1}{PAR} \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} E_d(\lambda) a^*_{pl,\,PSP}(\lambda) d\lambda; \tag{6}$$

PAR_0 and PAR – the respective total scalar and downward irradiances in the 400–700 nm spectral range:

$$PAR_0 = \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} E_0(\lambda) d\lambda \quad \text{and} \quad PAR = \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} E_d(\lambda) d\lambda. \tag{7}$$

Note that values of $f_a(\tau)$ can be determined from known chlorophyll-specific coefficients of light absorption by photosynthetic pigments ($\widetilde{a}^*_{pl,\,PSP}$) and by all phytoplankton pigments ($\widetilde{a}^*_{pl}$), averaged with the weight of the spectral distributions of the underwater irradiances. According to the definitions of these absorption coefficients (eqs. (5) and (6)), it is possible to determine them, provided that we have the following data:

- the spectrum of scalar irradiance $E_0(\lambda, z)$ and the total scalar irradiance in the 400–700 nm spectral range $PAR_0(z)$ at different depths in the sea (or the vector irradiance $PAR(z)$, as there is a simple, approximate relation between them: $PAR_0 \approx 1.2\, PAR$);
- the spectrum of the total absorption coefficients for all phytoplankton pigments $a_{pl}(\lambda, z)$ and for photosynthetic pigments $a_{pl,\,PSP}(\lambda, z)$, but only at the same depths as $E_0(\lambda, z)$.

On the other hand, values of $E_0(\lambda, z)$, $PAR_0(z)$ and $a^*_{pl}(\lambda, z)$, $a^*_{pl,\,PSP}(\lambda, z)$ can be determined from a knowledge of the surface irradiance $PAR_0(0)$ and the trophic index of the waters in question, i.e., the surface chlorophyll *a* concentration $C_a(0)$, using the following models:

- Woźniak's bio-optical model of the optical properties of the Baltic, with which typical scalar and vector irradiances can be determined for different trophic types of seawater and at different depths in the water column (Kaczmarek & Woźniak 1995, Woźniak et al. 2003);
- the model of the absorption properties of Baltic phytoplankton (Ficek et al. 2004) and also the model description of the vertical distribution of different pigment concentrations in the Baltic presented in parts 1 and 2 of this work (Ostrowska et al. 2007, Majchrowski et al. 2007, both in this volume). This enables spectra of the total absorption coefficients for all phytoplankton pigments and the absorption coefficient for photosynthetic phytoplankton pigments only to be determined.

3. Results and discussion

Within the framework of the foregoing analysis and modelling scheme, depth distributions of the factor f_a were determined by model calculations for a water layer extending from the surface down to an optical depth of $\tau \approx 5$ in Baltic waters of different trophic indices (from mesotrophic with a surface chlorophyll concentration $C_a(0) = 0.2$ mg tot. chl a m^{-3} to supereutrophic with $C_a(0) = 70$ mg tot. chl a m^{-3}) and for the various mean daily values of the irradiance just below the sea surface $PAR(0)$ (from close to 0 to 1600 μEin m^{-2} s^{-1}) measured in these waters. These calculations were performed independently for two seasons in the year: (1) the 'winter' period (from day in the year 1 to 118, and from 261 to 365) and (2) the 'summer' period (from day in the year 119 to 260). Hence, the calculations had to take into consideration the two mathematical descriptions, different for summer and winter, of the vertical distributions of the phytoplankton accessory pigment concentrations in the Baltic postulated in part 2 of this series (Majchrowski et al. 2007, this volume).

Some examples of the results obtained with reference to a mean daily irradiance of $PAR(0) = 600$ μEin m^{-2} s^{-1} are illustrated graphically in Figure 1b. This figure shows that values of f_a vary with depth in the sea and trophic index (surface concentration of chlorophyll $C_a(0)$); they also depend on the season of the year.

Comparison of these plots for the Baltic (Fig. 1b) with similar plots for oceanic waters (Fig. 1a) shows that they have certain features in common, like the increase in value of f_a with depth, but that there are also a number of differences between them. In particular, the dependence of f_a on trophic index, i.e., on the concentration $C_a(0)$, is more complex in the Baltic than in the oceans and more difficult to describe mathematically. This is because at the same optical depths in the sea and under the same irradiance conditions, the values of f_a measured in different regions of the Baltic (Fig. 1c) are usually the smallest in waters with an intermediate trophic index (values of $C_a(0)$ from 1.7 to 7.5 mg tot. chl a m^{-3}) and increase in waters of higher and lower trophic indices. The situation here is therefore different from that in oceanic Case 1 waters, where the value of f_a rises monotonically with increasing $C_a(0)$. Moreover, the range of variation of f_a in the Baltic (according our observations from 0.5 to 1) is narrower than that in oceanic waters. Finally, these changes in the Baltic exhibit a certain seasonality that was not detected in the oceans: the values of f_a under the same conditions measured in the 'warm' months (from May to September) are generally lower than in the remaining 'cool' months.

These values of f_a were obtained as a result of time-consuming calculations using the complex models described in Section 2 of this paper. To make the calculations easier, an alternative, polynomial method was developed to determine the mean absorption coefficients $\widetilde{a}^*_{pl}$, $\widetilde{a}^*_{pl,PSP}$, and then the factor f_a (from eq. (4)), from the surface total chlorophyll a concentration $C_a(0)$, the optical depth τ and the irradiance $PAR(0)$. To do this, the computed values of $\widetilde{a}^*_{pl}$, $\widetilde{a}^*_{pl,PSP}$ and f_a were approximated by means of a polynomial using the complete mathematical apparatus of earlier models.

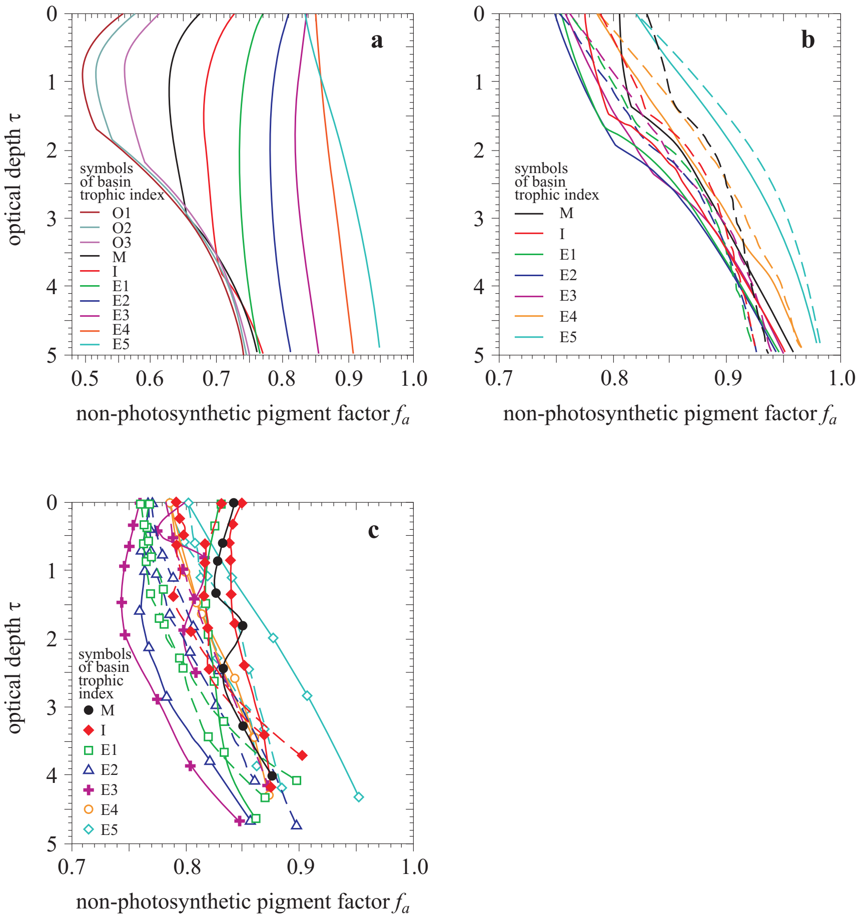

Figure 1. Vertical profiles of the non-photosynthetic pigment factor f_a in waters of different trophic index:

a) modelled profiles for $PAR(0) = 695$ μEin m^{-2} s^{-1} in oceanic Case 1 waters – according to Ficek et al. 2000;

b) modelled profiles for $PAR(0) = 600$ μEin m^{-2} s^{-1} in Baltic Case 2 waters; continuous lines – the 'winter' period (from day in the year 1 to 118 and from 261 to 365), dashed lines – the 'summer' period (from day in the year 119 to 260) according to formulas (1), (8), (9) and Tables 2 and 3;

c) empirical profiles in Baltic case 2 waters; continuous lines – the 'winter' period (from day in the year 1 to 118 and from 261 to 365), dashed lines – the 'summer' period (from day in the year 119 to 260); for the following trophic indices $C_a(0)$ given in [mg tot. chl *a* m^{-3}] and irradiance $PAR(0)$ given in [μEin m^{-2} s^{-1}]:
M – $C_a(0) = 0.42$; $PAR(0) = 304$; data from 17.02.2000;
I – $C_a(0) = 0.95$; $PAR(0) = 321$; data from 8.02.2003; $C_a(0) = 0.82$; $PAR(0) = 67$; data from 10.02.2003; $C_a(0) = 0.54$; $PAR(0) = 820$; data from 10.05.2000; (*continued next page*)

E1 – $C_a(0) = 1.04$; $PAR(0) = 270$; data from 03.2001; $C_a(0) = 1.38$; $PAR(0) = 810$; data from 9.05.2000; $C_a(0) = 1.62$; $PAR(0) = 855$; data from 23.05.2004;
E2 – $C_a(0) = 4.04$; $PAR(0) = 665$; data from 21.04.2004; $C_a(0) = 2.97$; $PAR(0) = 855$; data from 11.05.2000; $C_a(0) = 4.19$; $PAR(0) = 811$; data from 8.05.2002;
E3 – $C_a(0) = 5.25$; $PAR(0) = 381$; data from 10.04.2004; $C_a(0) = 5.26$; $PAR(0) = 654$; data from 22.04.2004; $C_a(0) = 5.86$; $PAR(0) = 691$; data from 16.09.2004;
E4 – $C_a(0) = 11.0$; $PAR(0) = 643$; data from 17.04.2004; $C_a(0) = 17.0$; $PAR(0) = 638$; data from 20.04.2004;
E5 – $C_a(0) = 22.6$; $PAR(0) = 667$; data from 19.04.2004; $C_a(0) = 22.7$; $PAR(0) = 330$; data from 27.04.1999; $C_a(0) = 32.6$; $PAR(0) = 690$; data from 28.04.1999

Table 1. Values of $A_{m,n}$ in eqs. (8) and (9)

a) 'winter' (for days in the year 1–118 and 261–365)

$n \backslash m$	0	1	2	3
0	1.921E–02	–1.323E–02	7.601E–03	–2.003E–03
1	–4.388E–03	4.326E–03	–1.655E–04	
2	4.319E–04	–8.490E–04		
3	9.279E–05			

b) 'summer' (for days in the year 119–260)

$n \backslash m$	0	1	2	3
0	2.059E–02	–2.019E–02	1.348E–02	–3.055E–03
1	–2.941E-03	5.189E–03	–1.246E–03	
2	1.633E–04	–4.930E–04		
3	2.641E–05			

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

a) 'winter' (for days in the year 1–118 and 261–365)

$n \backslash m$	0	1	2	3
0	2.836E–03	–4.004E–04	–1.808E–04	1.760E–05
1	–1.363E–04	–2.349E–04	1.750E–05	
2	–1.121E–04	4.973E–05		
3	1.332E–05			

b) 'summer' (for days in the year 119–260)

$n \backslash m$	0	1	2	3
0	2.788E–03	–3.302E–04	–2.138E–04	2.783E–05
1	–1.809E–04	–2.568E–04	2.268E–05	
2	–8.982E–05	5.022E–05		
3	1.124E–05			

Table 3. Values of $C_{m,n}$ in eq. (8)

a) 'winter' (for days in the year 1–118 and 261–365)

$n \backslash m$	0	1	2	3
0	4.680E–06	–2.074E–06	–2.582E–07	1.580E–08
1	–2.437E–06	1.247E–06	5.668E–08	
2	3.190E–07	–1.754E–07		
3	–2.155E–09			

b) 'summer' (for days in the year 119–260)

$n \backslash m$	0	1	2	3
0	4.576E–06	–1.941E–06	–3.052E–07	2.422E–08
1	–2.399E–06	1.173E–06	6.711E–08	
2	3.222E–07	–1.659E–07		
3	–3.622E–09			

The relevant values of $\widetilde{a}^*_{pl}$ and $\widetilde{a}^*_{pl,\,PSP}$ can be determined with the aid of polynomials (8) and (9). The values of the coefficients $A_{m,\,n}$, $B_{m,\,n}$ and $C_{m,n}$ are given in Tables 1–3. On the other hand, f_a was obtained according to eq. (4) by dividing $\widetilde{a}^*_{pl}$ and $\widetilde{a}^*_{pl,\,PSP}$ determined from the following polynomials:

$$\begin{aligned} \widetilde{a}^*_{pl} = & \sum_{m=0}^{3}\left[\sum_{n=0}^{3} A_{m,\,n}(\log(C_a(0)))^n\right]\tau^m + \\ & + \sum_{m=0}^{3}\left[\sum_{n=0}^{3} B_{m,\,n}(log(C_a(0)))^n\right]\tau^m + \\ & + PAR(0)\sum_{m=0}^{3}\left[\sum_{n=0}^{3} C_{m,\,n}(\log(C_a(0)))^n\right]\tau^m, \end{aligned} \tag{8}$$

$$\widetilde{a}^*_{pl,\,PSP} = \sum_{m=0}^{3}\left[\sum_{n=0}^{3} A_{m,\,n}(\log(C_a(0)))^n\right]\tau^m, \tag{9}$$

where
$C_a(0)$ [mg tot. chl a m^{-3}] – surface concentration of chlorophyll a;
$PAR(0)$ [μEin m^{-2} s^{-1}] – downward irradiance at the surface in the PAR spectral range (400–700 nm).

4. Verification of the model relationships; conclusions

Values of the factor f_a cannot be measured empirically. This is because it is impossible under in vivo conditions to measure separately the light absorption by photosynthetic pigments and by photoprotecting pigments. Such a measurement has so far been possible only with respect to the total absorption by all pigments. The verification of the values of f_a computed using the model description (see eqs. (4), (8) and (9)) was therefore based on quasi-empirical values of this factor. Such quasi-empirical values of f_a were calculated on the basis of empirical values of the following parameters measured at the same depths: $E_d(\lambda, z)$ (or also $PAR(z)$), $a_{pl}(\lambda, z)$ and the concentrations of all the groups of phytoplankton pigments $C_a(z)$ and $C_j(z)$ (where j denotes in turn chl b, chl c, PSC, $phyc$, PPC). This enabled the respective spectra of the chlorophyll-specific coefficient of light absorption for all phytoplankton pigments $a^*_{pl}(\lambda, z)$ and for photosynthetic pigments $a^*_{pl,PSP}(\lambda, z)$ to be calculated from generally known relationships (see, e.g., Woźniak & Dera 2007):

$$\begin{aligned} a^*_{pl}(\lambda, z) = (C_a(z))^{-1} Q^*(\lambda, z)[a^*_a(\lambda)C_a(z) + a^*_b(\lambda)C_b(z) + \\ + a^*_c(\lambda)C_c(z) + a^*_{PSC}(\lambda)C_{PSC}(z) + a^*_{phyc}(\lambda)C_{phyc}(z) + \\ + a^*_{PPC}(\lambda)C_{PPC}(z)], \end{aligned} \tag{10}$$

$$\begin{aligned} a^*_{pl,PSP}(\lambda, z) = (C_a(z))^{-1} Q^*(\lambda, z)[a^*_a(\lambda)C_a(z) + a^*_b(\lambda)C_b(z) + \\ + a^*_c(\lambda)C_c(z) + a^*_{PSC}(\lambda)C_{PSC}(z) + a^*_{phyc}(\lambda)C_{phyc}(z)], \end{aligned} \tag{11}$$

where

a^*_a, a^*_b, a^*_c, a^*_{PSC}, a^*_{phyc}, a^*_{PPC} – the respective spectral mass-specific absorption coefficients of light for chlorophylls a, chlorophylls b, chlorophylls c, photosynthetic carotenoids (PSC), phycobilins and photoprotecting carotenoids (PPC) (in solvent). In the calculations the values of these coefficients are those typical of the pigments in Baltic phytoplankton, determined earlier and described by the sum of Gaussian bands (see eqs. (4) and (5), and Table 2 in Ficek et al. 2004);

$Q^*(\lambda, z)$ – a spectral dimensionless factor of the change in absorption due to pigment packaging in the phytoplankton cells, the so-called packaging function (Hulst 1981, Morel & Bricaud 1981, Woźniak & Dera 2007). The values of this packaging function were calculated by the method of successive approximations based on known empirical spectra of $a_{pl}(\lambda, z)$ and empirically determined data on the concentration of pigments $C_j(z)$. The algorithm of such approximate calculations is presented in the Annex in Woźniak et al. 1999.

Once the spectra of $a^*_{pl}(\lambda, z)$ and $a^*_{pl,PSP}(\lambda, z)$ were established, their mean values (according to eqs. (5) and (6)), weighted by the downward irradiance spectra $E_d(\lambda, z)$ measured empirically at the same depths z, could be defined. Then, according to eq. (4), the quasi-empirical values of the non-photosynthetic pigment factor – $f_{a,\,D}(z)$ (determined quasi-empirically – index D) were calculated.

A total of 400 values of the quasi-empirical non-photosynthetic pigment absorption factor $f_{a,\,D}(z)$ were determined in the above manner at different depths in the sea over a range of optical depths from $\tau = 0$ to 5 at 50 measuring stations. Figure 1c illustrates examples of such empirical profiles of $f_a(\tau)$. Then, the values of $f_{a,\,C}$ (computed using model – index C) computed for these stations and depths using eqs. (8), (9) and (4) were compared with those determined quasi-empirically $f_{a,\,D}$. Figure 2 compares these modelled and measured values, and Table 4 gives the errors of the estimation.

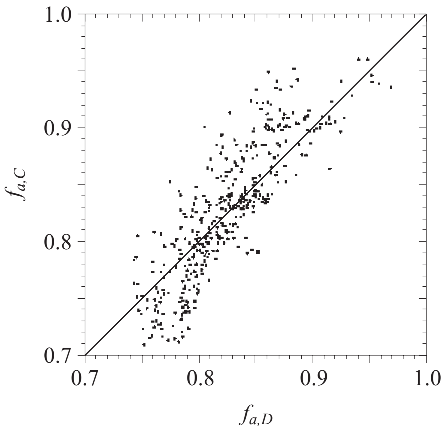

Figure 2. Comparison of the values of the empirical non-photosynthetic pigment absorption factor $f_{a,\,D}$ with the corresponding values calculated by the polynomial method $f_{a,\,C}$ (using formulas (8), (9) and (4)) in the euphotic zone of the Baltic at different stations in 1999–2004

These plots and the verification show that the errors in the values of the non-photosynthetic pigment absorption factor f_a estimated using the model developed in this work (eqs. (4), (8) and (9)) are small: in practice they do not exceed 4%. Likewise, the changes of these model values of f_a in Baltic waters of different trophic indices with depth (Fig. 1b) are similar in range and nature, as are the empirical profiles (Fig. 1c). This testifies to the practical utility of this mathematical description of the vertical distribution of the non-photosynthetic pigment absorption factor. The objective of this work has therefore been achieved. These new mathematical expressions, enabling vertical profiles of the factor f_a in the Baltic to be estimated from known trophic indices ($C_a(0)$) and surface irradiances ($E_d(\lambda, 0)$ and/or $PAR(0)$), can be successfully applied in remote-sensing algorithms for monitoring the Baltic ecosystem.

Table 4. Relative errors in the estimation with formulas (8), (9) and (4) of the non-photosynthetic pigment absorption factor $f_{a,C}$ in the euphotic zone of the Baltic Sea.

Arithmetic statistics		Logarithmic statistics			
systematic error $<\varepsilon>$ [%]	statistical error σ_ε [%]	systematic error $<\varepsilon>_{\mathrm{g}}$ [%]	standard error factor x	statistical error σ_- [%]	σ_+ [%]
0.06	$\pm$3.96	–0.01	1.04	–3.87	+4.03

where

$\varepsilon = (f_{a,C} - f_{a,D})$ – relative error,

$f_{a,D}$ quasi-empirical non-photosynthetic pigment absorption factor – (eqs. (10), (11) and (4)),

$f_{a,C}$ modelled non-photosynthetic pigment absorption factor (eqs. (8), (9) and (4)),

$<\varepsilon>$ – arithmetic mean error,

σ_ε – standard deviation of errors (statistical error),

$<\varepsilon>_{\mathrm{g}} = 10^{[<\log(f_{a,C}/f_{a,D})>]} - 1$ – logarithmic mean of errors,

$<\log(f_{a,C}/f_{a,D})>$ – mean of $\log(f_{a,C}/f_{a,D})$,

$\sigma_{\log}$ – standard deviation of $\log(f_{a,C}/f_{a,D})$,

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

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

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