Remote sensing of vertical phytoplankton pigment distributions in the Baltic: new mathematical expressions. Part 2: Accessory pigment distribution*

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Abstract

This is the second in a series of articles, the aim of which is to derive mathematical expressions describing the vertical distributions of the concentrations of different groups of phytoplankton pigments; these expressions are necessary in the algorithms for the remote sensing of the marine ecosystem. It presents

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formulas for the vertical profiles of the following groups of accessory phytoplankton pigments: chlorophylls b, chlorophylls c, phycobilins, photosynthetic carotenoids and photoprotecting carotenoids, all for the uppermost layer of water in the Baltic Sea with an optical depth of $\tau \approx 5$. The mathematical expressions for the first four of these five groups of pigments, classified as photosynthetic pigments, enable their concentrations to be estimated at different optical depths in the sea from known surface concentrations of chlorophyll a. The precision of these estimates is characterised by the following relative statistical errors according to logarithmic statistics σ_-: approximately 44% for chlorophyll b, approx. 39% for chlorophyll c, approx. 43% for phycobilins and approx. 45% for photosynthetic carotenoids. On the other hand, the mathematical expressions describing the vertical distributions of photoprotecting carotenoid concentrations enable these to be estimated at different depths in the sea also from known surface concentrations of chlorophyll a, but additionally from known values of the irradiance in the PAR spectral range at the sea surface, with a statistical error σ_- of approximately 42%.

1. Introduction

This article is the second in a series of three, whose objective was to find mathematical formulas to describe the vertical distributions of phytoplankton pigments in the Baltic Sea, formulas that would be useful in algorithms applied in the remote monitoring (mostly by satellite) of the Baltic ecosystem. The first article in this series (see Ostrowska et al. (2007), this volume) presented a mathematical description of the vertical distribution of the total chlorophyll a concentration in the Baltic. The model formula given there enables the chlorophyll a concentration at different depths in the Baltic Sea $C_a(z)$[1] to be estimated from known surface concentrations of this pigment $C_a(0)$, which can be defined by remote-sensing techniques (e.g., Ruddick et al. 2000, Sathyendranath 2001, Darecki et al. 2003). In the present article the focus is on equivalent mathematical descriptions of the resources and spatial distributions of the accessory pigments in Baltic phytoplankton.

The compositions and concentrations of phytoplankton pigments at different depths in seawaters of different trophic index[2] vary widely (see

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

[2]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).

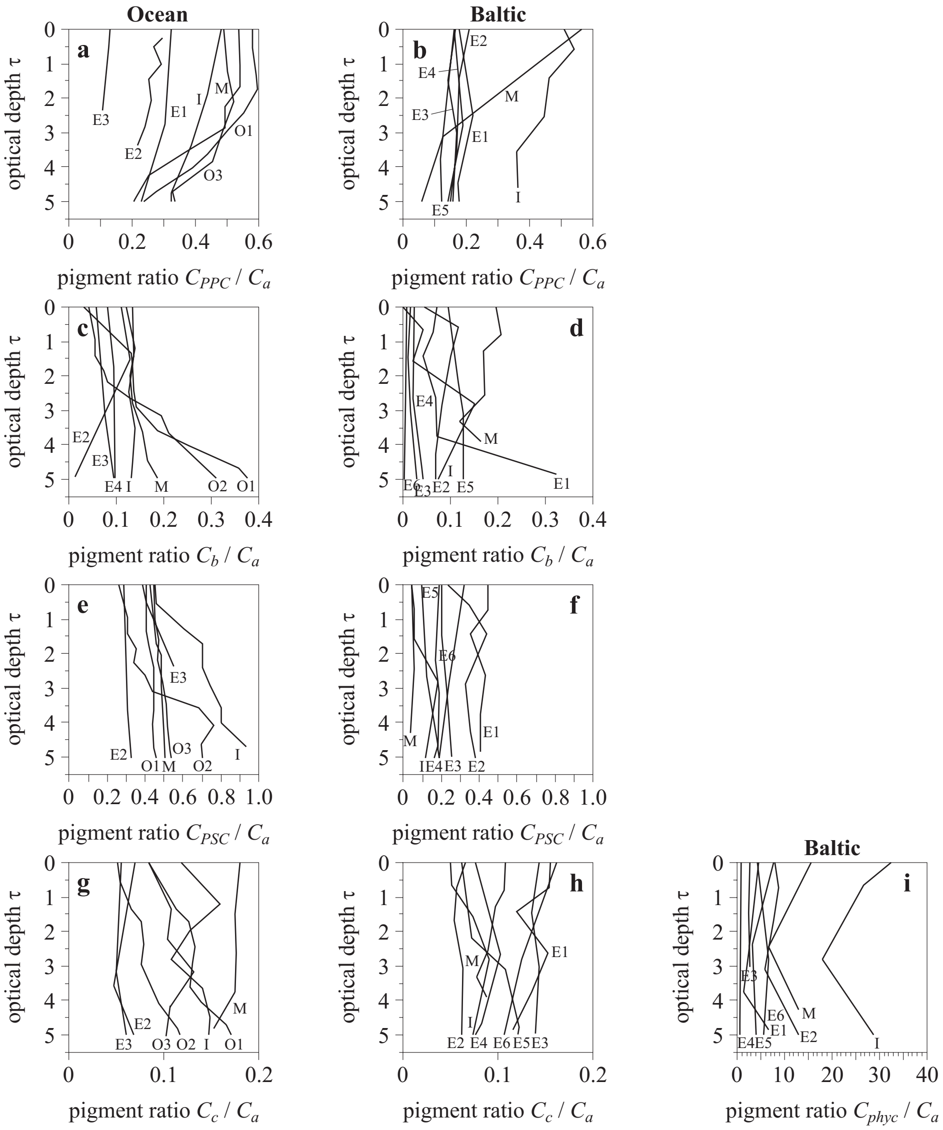

Figure 1. Vertical distributions of measured concentrations of pigments relative to chlorophyll a, in different trophic types of waters in seas and oceans containing waters approximating to Case 1 waters (a, c, e, g) and in the Baltic Sea (b, d, f, h, i). The separate figures refer to: photoprotecting carotenoids PPC (a, b), chlorophylls b (c, d), photosynthetic carotenoids PSC (e, f), chlorophylls c (g, h) and phycobilins (i). The symbols on the figure denote the various trophic types of water in accordance with the classification in footnote 2

Figure 1). The absolute concentrations of these pigments are known to depend in large measure on the trophic index of the waters in question, which is the principal factor regulating the magnitude of phytoplankton resources in the sea (Steemann Nielsen 1975, Babin et al. 1996, Woźniak & Dera 2007). On the other hand, the composition of these various phytoplankton pigments, i.e., the mutual relations between their concentrations, is governed largely by the irradiance conditions in the water. It is these that determine the light adaptation processes taking place in phytoplankton cells, and the light acclimation occurring at the phytocoenosis level that leads to changes in the species composition of the phytoplankton. These processes of light acclimation and adaptation lead to the earlier-mentioned differentiation in pigment compositions observed at different depths in different types of seas (Babin et al. 1996, Majchrowski 2001).

The processes by which single organisms (as a result of internal changes) or entire phytocoenoses (as a result of changes in the species composition) adapt to light factors may be of two kinds:

1) photoacclimation (or photo-adaptation), which gives rise to changes in the relative concentrations of photoprotecting pigments C_{PPC}/C_a, i.e., relative to the concentration of chlorophyll a, C_a, at given depths and in given types of waters. These photoprotecting pigments are primarily the following carotenoid pigments: diadinoxanthin, alloxanthin, zeaxanthin, lutein, neoxanthin, violaxanthin, diatoxanthin, myxoxanthophyll, antheraxanthin, β-carotene. The role of these photoprotecting pigment molecules is mainly to capture part of the excitation energy of chlorophyll a; this prevents its photooxidation. The mechanisms of these processes have been described in, e.g., Grodziński (1978), Majchrowski (2001) and Woźniak & Dera (2007);

2) chromatic acclimation (or chromatic adaptation), which gives rise to changes in the concentrations of accessory antenna pigments (photosynthetic pigments) relative to the concentration of chlorophyll a, C_a, i.e., the relative concentrations of chlorophyll b (C_b/C_a), chlorophyll c (C_c/C_a), photosynthetic carotenoids like fucoxanthin, peridinin, α-carotene, prasinoxanthin, 19'butanoyloxyfucoxanthin and 19'hexanoyloxyfucoxanthin (C_{PSC}/C_a), phycobilins (C_{phyc}/C_a) and others. It is the role of these accessory photosynthetic pigments to obtain light energy for photosynthesis mainly from those spectral intervals in which chlorophyll a is a poor absorber. This follows from the absorption of light quanta by molecules of these pigments and the transfer of this absorbed energy to chlorophyll a molecules. This question is discussed at length, e.g., in Govindjee (1975), Majchrowski (2001), and Woźniak & Dera (2007).

In our earlier publications (Woźniak et al. 1997a,b, 2003, Majchrowski et al. 1998, Majchrowski & Ostrowska 1999, 2000) a mathematical description was presented of the effects of both these kinds of adaptation of phytoplankton to the irradiance conditions prevailing in ocean basins. In particular, mathematical expressions were derived describing the dependence of the relative concentrations of photoprotecting pigments C_{PPP}/C_a and photosynthetic pigments C_{PSP}/C_a on various irradiance characteristics in the sea. In the case of photo-adaptation, we found that the factor governing this process quantitatively was the Potentially Destructive Radiation (PDR), defined as follows:

$$PDR^* = \int_{400\,\mathrm{nm}}^{480\,\mathrm{nm}} a_a^*(\lambda)\ \langle E_0(\lambda)\rangle_{\mathrm{day}}\, d\lambda, \tag{1}$$

where

PDR^* – the potentially destructive radiation per unit mass of chlorophyll a (the asterisk indicates that this is the PDR per unit mass of chlorophyll a) [μEin (mg chl a)$^{-1}$ s^{-1}];

$a_a^*(\lambda)$ – the specific coefficient of light absorption by chlorophyll a [m^2 (mg tot. chl a)$^{-1}$];

$\langle E_0(\lambda)\rangle$ – the scalar irradiance in the medium – $< E_0(\lambda) >_{\mathrm{day}}$ stands for the mean daily value of this irradiance typical of a given season, region and depth in the sea [μEin m^{-2} s^{-1} nm^{-1}].

The magnitude of PDR^* is equal to the energy from the blue spectral region (400–480 nm) which can be absorbed by chlorophyll a and which could cause this pigment to photo-oxidise. It turns out that this magnitude of PDR^* correlates well with the relative concentration of photoprotecting carotenoids in phytoplankton, if its mean value is taken for a water layer Δz from 30 m to 60 m thick (see explanation in eq. (3)) in order to allow for the vertical migration of phytoplankton as a result of water mixing. This interrelationship is expressed by the following formula (Majchrowski 2001, Woźniak et al. 2003):

$$C_{PPC}/C_a = 0.1758 \times < PDR^* >_{\Delta z} +0.176, \tag{2}$$

where

$$< PDR^* >_{\Delta z} = \frac{1}{z_2 - z_1} \int_{z_1}^{z_2} PDR^*(z) dz. \tag{3}$$

The thicknesses of the water layers are defined as follows: $\Delta z = z_2 - z_1$, where $z_2 = z + 30$ m and $z_1 = 0$ if $z < 30$ m, or $z_1 = z - 30$ m if $z \geq 30$ m.

Now, our studies of chromatic adaptation processes have shown that magnitudes well correlated with the relative concentrations of the various groups of photosynthetic pigments are the so-called spectral fitting functions F_j (dimensionless) for the j^{th} pigment, known as chromatic adaptation factors. They have been defined as follows:

– for chlorophyll a:

$$F_a = \frac{1}{a^*_{a,\,\max}} \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} f(\lambda)\ a^*_a(\lambda) d\lambda, \tag{4a}$$

– for photosynthetic carotenoids PSC:

$$F_{PSC} = \frac{1}{a^*_{PSC,\,\max}} \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} f(\lambda)\ a^*_{PSC}(\lambda) d\lambda, \tag{4b}$$

– for chlorophyll b:

$$F_b = \frac{1}{a^*_{b,\,\max}} \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} f(\lambda)\ a^*_b(\lambda) d\lambda, \tag{4c}$$

– for chlorophyll c:

$$F_c = \frac{1}{a^*_{c,\,\max}} \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} f(\lambda)\ a^*_c(\lambda) d\lambda, \tag{4d}$$

where

$a^*_a(\lambda)$, $a^*_{PSC}(\lambda)$, $a^*_b(\lambda)$, $a^*_c(\lambda)$ – the specific coefficients of absorption by chlorophyll a, PSC, chlorophyll b and chlorophyll c [$\mathrm{m}^2(\mathrm{mg\,pigment})^{-1}$] respectively;

$a^*_{a,\,\max}$, $a^*_{PSC,\,\max}$, $a^*_{b,\,\max}$, $a^*_{c,\,\max}$ – the respective values of these specific coefficients in the maximum absorption bands for chlorophyll a, PSC, chlorophyll b and chlorophyll c;

$f(\lambda) = E_d(\lambda)/PAR$ – the spectral function of the downward irradiance distribution in the PAR range [nm^{-1}].

On the other hand, the statistical relationships established between the relative concentrations of the various pigment groups in oceanic waters and the above-mentioned spectral fitting functions, averaged in the water layers Δz (defined above) to take account of mixing processes, are the following (Majchrowski 2001, Woźniak et al. 2003):

– photosynthetic carotenoids PSC:

$$C_{PSC}/C_a = 1.348 \times < F_{PSC} >_{\Delta z} -0.093, \tag{5a}$$

– chlorophyll b:

$$C_b/C_a = 54.068 \times < F_b >_{\Delta z}^{5.157} + 0.091, \tag{5b}$$

– chlorophyll c:

$$C_c/C_a = 0.0424 \times < F_c >_{\Delta z} < F_a >_{\Delta z}^{-1.197}, \tag{5c}$$

where the fitting functions F_j (where j denotes in turn photosynthetic carotenoids, chlorophylls b, chlorophylls c and chlorophylls a) are averaged:

$$< F_j >_{\Delta z} = \frac{1}{z_2 - z_1} \int_{z_1}^{z_2} F_j(z) dz \tag{6}$$

and where the thicknesses of the water layers are defined as in eq. (3).

Here the phycobilins have been omitted: they are found only in a few rare species of algae, so occur only sporadically. For all practical purposes they can be regarded as absent from oceanic phytoplankton.

The above mathematical formulas defining the relative concentrations of the various groups of photoprotecting (PPC, see eqs. (1)–(3)) and photosynthetic pigments (chl b, chl c and PSC, see eqs. (4)–(6)) enable these concentrations to be determined from known concentrations of chlorophyll a and the irradiance conditions in the sea. These formulas were verified empirically by their application to the distributions of pigment concentrations in oceanic waters – the results were positive (Woźniak et al. 2003, Ficek et al. 2003). However, our attempts to apply the oceanic version of these model formulas to describe the distribution of pigment concentrations in Baltic waters were unsuccessful. This persuaded us to search for and develop alternative model formulas for the Baltic Sea based on statistical analyses of empirical material gathered in these waters. The aim of the present article is, therefore, to present this modelling process and the model formulas established for the Baltic, as was done above for oceanic waters. It should be mentioned that the mathematical description of pigment concentrations that follows will include a term to account for the concentrations of phycobilins, which may be far more common in Baltic than in oceanic phytoplankton.

2. The empirical material: characteristics

In order to achieve the objectives of this work, empirical data gathered in various regions of the Baltic Sea during cruises of r/v 'Oceania' (IO PAS[3] Sopot) and r/v 'Baltica' (MIR[4] Gdynia) in 1999–2004 were

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employed. This bank of empirical data contained a large number of different marine environmental parameters and magnitudes characterising the various properties of phytoplankton and photosynthesis. Of these parameters, the following, measured at different depths at more than 200 stations, were used in the present analysis:

- the concentrations of different phytoplankton pigments from the following groups: chlorophylls, carotenoids and phycobilins, $C_j(z)$ [mg j-pigment m^{-3}];
- the spectra of light absorption by phytoplankton, $a_{pl}(\lambda, z)$ [m^{-1}];
- the spectra of downward irradiance in the PAR spectral range (400–700 nm), $E_d(\lambda, z)$ [μEin m^{-2} s^{-1} nm^{-1}] and the total downward irradiance in this range, $PAR(z)$ [μEin m^{-2} s^{-2}].

The details of these data for individual months and years are listed in Table 1. The total number of empirical data sets containing concentrations of selected pigment groups C_j and absorption spectra $a_{pl}(\lambda)$ is 1568; 881 of these contain the concentrations of all the pigment groups, all the spectra $a_{pl}(\lambda)$ and also the spectra $E_d(\lambda)$.

Table 1. Details of the empirical database – total number of measurement sets (1568) (C_j, $a_{pl}(\lambda)$); in parentheses the total number of complete measurement sets (881) (C_j, $a_{pl}(\lambda)$, $E_d(\lambda)$) (see text)

Month	1999	2000	2001	2002	2003	2004	Total
January							
February		44 (36)	26 (26)		72 (38)	48 (33)	190 (133)
March	34	22 (14)		45	84		185 (14)
April	115 (115)			5	32 (15)	99 (96)	251 (226)
May		53 (50)	94	70 (36)	20 (20)	106 (91)	343 (197)
June					83	43 (11)	126 (11)
July					13	22 (22)	35 (22)
August					23 (23)	10	33 (23)
September	40	91 (87)	43 (42)		54 (54)	73 (72)	301 (255)
October				5		43	48
November				16	9	13	38
December					18		18
Total	**189 (115)**	**210 (187)**	**163 (68)**	**141 (36)**	**408 (150)**	**457 (325)**	**1568 (881)**

2.1. Methodology of estimating the concentrations of pigments from the chlorophyll and carotenoid groups

The concentrations of pigments from the chlorophyll group (chlorophylls a: divinyl chl a, allomer chl a, epimer chl a; chlorophyll b; chlorophylls c: chl $c1 + c2$, chl $c3$) and the carotenoid group (including diadinoxanthin, alloxanthin, zeaxanthin, lutein, neoxanthin, violaxanthin, diatoxanthin, myxoxanthophyll, antheraxanthin, β-carotene, fucoxanthin, peridinin, α-carotene, prasinoxanthin, 19'but-fucoxanthin, 19'hex-fucoxanthin, echinenone) in water samples drawn from different depths in the sea were determined by HPLC (Mantoura & Llewellyn 1983). The apparatus and the details of these techniques in the version applied at IO PAS are described in, e.g., Stoń & Kosakowska (2002), Stoń-Egiert & Kosakowska (2005) and Ficek et al. (2003). From these measurements of the different forms of chlorophyll a, summation yielded the total concentration of chlorophyll a, C_a [mg tot. chl a m^{-3}], the total concentrations of chlorophylls b, C_b [mg chl b m^{-3}], and chlorophylls c, C_c [mg chl c m^{-3}], were obtained in the same way. The identified compounds in the carotenoid groups were classified into two subgroups on the basis of the different roles they play in the photosynthetic apparatus: photosynthetic carotenoids (PSC) and photoprotecting carotenoids (PPC). The PSC group includes β-carotene, fucoxanthin, peridinin, α-carotene, prasinoxanthin, 19'but-fucoxanthin, 19'hex-fucoxanthin and echinenone; the PPC group contains diadinoxanthin, alloxanthin, zeaxanthin, lutein, neoxanthin, violaxanthin, diatoxanthin, myxoxanthophyll, antheraxanthin and β-carotene. Summation of the concentrations of the compounds classified into the same subgroups (PSC and PPC) yields their total concentrations, i.e., C_{PSC} [mg PSC m^{-3}] and C_{PPC} [mg PPC m^{-3}]. These totals include the approximate contents of unidentified carotenoids (usually $< 10\%$); it was assumed here that the ratio of the concentrations of unidentified PSC to unidentified PPC is roughly the same as the ratio of the concentrations of identified PSC to identified PPC.

2.2. Method of estimating phycobilin concentrations

Phycobilins are often characteristic pigments in Baltic phytoplankton. Knowledge of their concentrations in Baltic phytoplankton therefore appears to be indispensable; it is of considerable importance for the calculation of coefficients of light absorption by Baltic algae and as a result may affect the precision with which the magnitude of primary production in the Baltic is estimated. However, neither the HPLC technique that was used to define pigment concentrations in algal cells, nor the other traditional methods used in oceanography to determine them are applicable to phycobilins: none of these methods is capable of identifying phycobilins. But there is an indirect way of estimating concentrations of unidentified pigments C_{UP}.

Such an optical method of indirectly estimating C_{UP} is based on a comparison of measured spectra of coefficients of the total absorption of light by algae $a_{pl}(\lambda)$ (i.e., by all the phytoplankton pigments – the various chlorophylls, carotenoids and phycobilins) with the light absorption spectra of identified pigments only $a_{pl-UP}(\lambda)$ (i.e., total phytoplankton absorption minus unrecorded pigments), estimated using the model. Such model spectra of $a_{pl-UP}(\lambda)$ can be obtained by applying the model of light absorption spectra by Baltic algae that was developed earlier and presented in Ficek et al. (2004). In accordance with this model, the formula for estimating the approximate concentrations of unidentified pigments C_{UP} (mainly phycobilins, as shown in Ficek et al. (2004)) can be written as follows:

$$\left.\begin{aligned} C_{phyc} \approx C_{UP} &= \frac{\displaystyle\int_{450\,\mathrm{nm}}^{630\,\mathrm{nm}} \left[\frac{a_{pl}(\lambda)}{Q^*(\lambda)} - a_{pl-UP,\,s}(\lambda)\right] d\lambda}{\displaystyle\int_{450\,\mathrm{nm}}^{630\,\mathrm{nm}} a^*_{UP}(\lambda) d\lambda} \\ a_{pl-UP,\,s}(\lambda) &= \sum_j C_j(\lambda) \times a^*_j(\lambda) \end{aligned}\right\}, \qquad (7)$$

where

$a_{pl}(\lambda)$ – the empirical coefficient of light absorption by phytoplankton;

$Q^*(\lambda)$ – the spectral packaging function, dependent on the chlorophyll a concentration C_a; it is a dimensionless factor representing the change in absorption due to pigment packaging in the phytoplankton cells (Hulst 1981). Its mathematical description is given in Ficek et al. (2004) – see the set of eqs. (3), (4) and (7) in that paper;

$a_{pl-UP,\,s}(\lambda)$ – the model coefficient of light absorption by all the phytoplankton pigments in the unpackaged ('in solvent') state except the unidentified ones;

$a^*_{UP}(\lambda)$, $a^*_j(\lambda)$ – the respective specific, model coefficients of light absorption by unidentified pigments (mainly phycobilins, as was assumed) and by identified pigments. The mathematical description of all these spectra a^*_{UP}, a^*_j as a sum of Gaussian bands is given in Ficek et al. (2004) – see also eqs. (4) and (5) and Table 2 in that paper;

j – an index denoting the principal group of pigments – chl a (a), chl b (b), chl c (c), photosynthetic carotenoids (PSC), photoprotecting carotenoids (PPC).

Applying this formula to the determination of approximate phycobilin concentrations C_{phyc} requires a knowledge of the complete empirical data set, which includes the empirical spectra of light absorption by phytoplankton a_{pl} and the concentrations of the principal pigment groups C_j (chl a, chl b, chl c, PSC, PPC) as measured by HPLC.

2.3. Optical measurement techniques

The daily distribution of downward spectral irradiance $E_d(\lambda, z, t)$ and the total irradiance in the photosynthetically available radiation spectral range $PAR(z)$ (from c. 400 nm to 700 nm) were measured optically in situ using the following underwater spectrophotometers: MER 2040 (up to 2003), RAMSESE ACC Hyperspectral Radiometers (in 2003 and 2004). The physical principles underlying these measurements are explained in, e.g., Dera (1971), Woźniak & Montwiłł (1973) and Woźniak et al. (1983).

The spectral coefficients of light absorption by phytoplankton in the spectral range 350–750 nm were measured in vivo using non-extraction methods (see, e.g., Tassan & Ferrari (1995, 2002), Ferrari & Tassan (1999)) in suitably prepared samples of water containing phytoplankton, drawn from different depths in the sea. The relevant spectral measurements were performed on a UNICAM UV4-100 spectrophotometer equipped with a LABSPHERE RSA-UC-40 integrating sphere. This is described in detail in Ficek et al. (2004).

Besides these two optical characteristics, the statistical analyses also took other optical magnitudes into account, which were determined indirectly on the basis of the above-mentioned ones. They were:

- the optical depth in the sea $\tau(z)$ [dimensionless], determined from measurements of the $PAR(z)$ irradiance at different depths in the sea using the well-known relationship:

$$\tau(z) = \ln(PAR(0)/PAR(z)); \tag{8}$$

- the potentially destructive radiation per unit of total chlorophyll a mass $PDR^*(z)$ at different depths in the sea – determined using eq. (1);
- the spectral fitting functions for the several groups of pigments – F_a, F_b, F_c, F_{PSC} – determined from eqs. (4a)–(4d).

3. The analyses – methods and results

The empirical material presented in the previous section was subjected to statistical analysis. To begin with, the agreement between the oceanic model and in situ measurements of the concentrations of the principal pigment groups relative to the chlorophyll a concentration C_a was tested, i.e., C_b/C_a, C_c/C_a, C_{PSC}/C_a and C_{PPC}/C_a, as estimated using the set of mathematical formulas established for oceanic waters (the oceanic model – see eqs. (1)–(6)). To do this, the empirical absolute values of these concentrations at different depths in the Baltic Sea were compared with their values estimated using the oceanic model, and the relevant errors of these estimations were determined. To convert these estimated relative concentrations C_j/C_a into the absolute concentrations of the several j^{th} pigments C_j, the formula for estimating the total vertical distribution of chlorophyll a, as modified for the Baltic, was used; this is described in part 1 of this series of articles (Ostrowska et al. 2007, this volume; see eq. (1) in that paper).

Since, however, the results using this first method were unsatisfactory – they were encumbered with large errors – the second stage of this work was embarked upon, the aim of which was to find new model descriptions, different from those in the oceanic model, of the vertical distribution of pigment concentrations for the Baltic Sea. These new model descriptions were restricted to the uppermost layer of the sea with an optical depth of $\tau \approx 5$. Nonetheless, such a layer is thicker than the depth to which PAR (1%) irradiance is able to penetrate and corresponds roughly to the thickness of the euphotic zone ($\tau_{1\%} \approx 4.6$).

3.1. Baltic model formula for calculating the vertical profiles of photoprotecting carotenoid (PPC) concentrations

The analyses showed that, as in the case of oceanic waters, the factor governing the PPC content in Baltic phytoplankton is the magnitude of the Potentially Destructive Radiation per unit of the total chlorophyll a mass, $PDR^*(z)$. But direct application of the oceanic version of the relationship between C_{PPC}/C_a and $< PDR^* >_{\Delta z}$ (see eqs. (2) and (3)) for determining the concentration C_{PPC} in the Baltic produces fairly large errors, as shown in Table 2 (item 2). This table also lists the errors in estimating C_{PPC} using this oceanic formula with respect to the carotenoids in the oceans (item 1). Clearly, the errors are much larger in the case of Baltic phytoplankton than for oceanic algae; in particular, the large systematic errors are highly unsatisfactory. Therefore, a different formula is needed for the Baltic, which more closely approximates the empirical relationship of C_{PPC}/C_a versus $< PDR^* >_{\Delta z}$ (see Figures 2a and 2b); in this work this was established by means of linear regression. In the search for this formula, a number of factors were changed, e.g., the thickness of the mixing water layer Δz. The best results were obtained for a mixing layer thinner than that in the ocean, the thickness being set at between 15 m (at the surface) and 30 m (for $z > 15$ m). The following model relationship was finally obtained:

$$C_{PPC}/C_a = 0.164 \times < PDR^* >_{\Delta z} + 0.164, \tag{9}$$

where

$$< PDR^* >_{\Delta z} = \frac{1}{z_2 - z_1} \int_{z_1}^{z_2} PDR^*(z) dz \tag{10}$$

and $\Delta z = z_2 - z_1$, where $z_2 = z + 15$ m and $z_1 = 0$ if $z < 15$ m, or $z_1 = z - 15$ m if $z \geq 15$ m.

Table 2. Errors in the estimation of photoprotecting carotenoids C_{PPC} using:
1 – the oceanic model (eq. (3)) in the oceans (after Majchrowski & Ostrowska (2000))
2 – the oceanic model (eq. (3)) in the Baltic
3 – the Baltic model (eq. (9)) in the Baltic

	Arithmetic statistics		Logarithmic statistics			
	systematic error	statistical error	systematic error	standard error factor	statistical error	
Item	$< \varepsilon >$ [%]	σ_ε [%]	$< \varepsilon >_{\mathrm{g}}$ [%]	x	σ_- [%]	σ_+ [%]
1	7.80	± 45.0	–0.22	1.47	–32.4	47.2
2	38.0	± 85.1	17.9	1.735	–42.3	73.5
3	16.8	± 72.8	–0.196	1.732	–42.3	73.2

where
$\varepsilon = (C_{PPC,\,C} - C_{PPC,\,M})/C_{PPC,\,M}$ – relative error;
$C_{PPC,\,C}$, $C_{PPC,\,M}$ – concentrations of photoprotecting carotenoids measured (index M) and determined using formulas (2) and (9) (index C),
$< \varepsilon >$ – arithmetic mean of errors,
σ_ε – standard deviation of errors (statistical error),
$< \varepsilon >_{\mathrm{g}} = 10^{[< \log(C_{PPC,\,C}/C_{PPC,\,M}) >]} - 1$ – logarithmic mean of errors,
$< \log(C_{PPC,\,C}/C_{PPC,\,M}) >$ – mean of $\log(C_{PPC,\,C}/C_{PPC,\,M})$,
$\sigma_{\log}$ – standard deviation of $\log(C_{PPC,\,C}/C_{PPC,\,M})$,
$x = 10^{\sigma_{\log}}$ – standard error factor,
$\sigma_- = \frac{1}{x} - 1$ and $\sigma_+ = x - 1$.

As Figures 2a and 2b show, this dependence of the concentration ratio C_{PPC}/C_a on the potentially destructive radiation PDR^* is weak; values are very widely scattered. Over the wide range of values of PDR^* measured in the sea, in particular those $< 10^{-1}$ μEin (mg tot. chl a)$^{-1}$ s^{-1}, relative PPC concentrations C_{PPC}/C_a are practically independent of this radiation. In practice, only for values of $PDR^* > 10^{-1}$ μEin (mg tot. chl a)$^{-1}$ s^{-1} does a tendency for relative PPC concentrations to rise become detectable. Hence, in the Baltic, as in the oceans, PPC contents are highest in well irradiated water layers, i.e., close to the sea surface, where PDR^* takes large values (Fig. 2d), but decline with increasing depth. It is also for this reason that PPC contents are higher in waters of a lower trophic index than in more eutrophic waters. The algae in the former, which sunlight (and hence

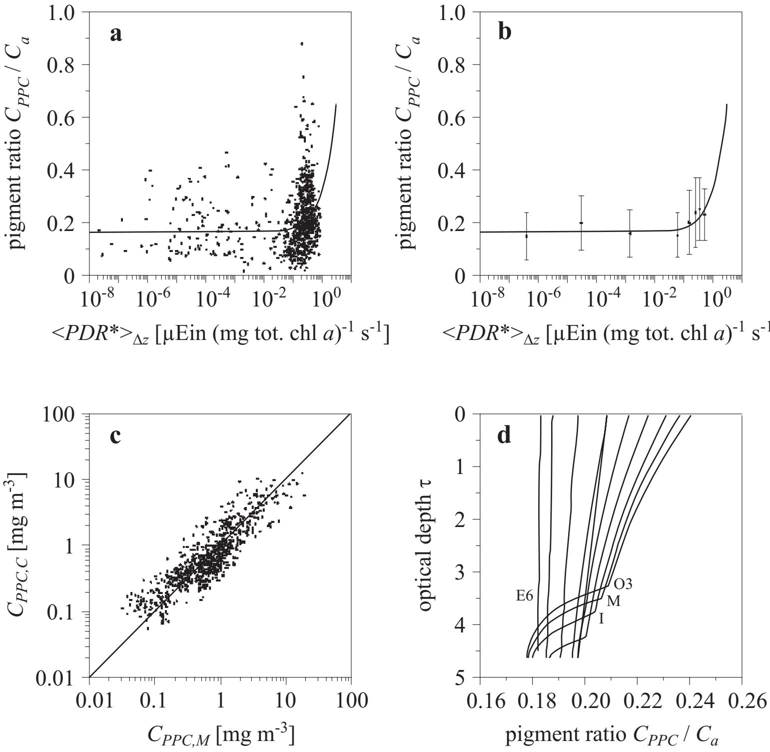

Figure 2. Statistical relationship between the relative concentrations of photoprotecting carotenoids C_{PPC}/C_a and the mean value of the Potentially Destructive Radiation $< PDR^* >_{\Delta z}$ in the mixing layer $\Delta z \pm 15$ m (points – empirical data, line – approximation using formula (9)) (a); mean values and standard deviations for the dependence of relative concentrations of photoprotecting carotenoids C_{PPC}/C_a on $< PDR^* >_{\Delta z}$ (points – mean values, line – approximation using formula (9)) (b); comparison of empirical $C_{PPC,\,M}$ and model $C_{PPC,\,C}$ PPC concentrations according to formula (9), at different stations and depths in the Baltic Sea (c); model vertical distributions of the relative concentrations of photoprotecting carotenoids C_{PPC}/C_a as a function of the optical depth τ in different trophic types of Baltic waters (d). The symbols on the figure denote the various trophic types of water in accordance with the classification in footnote 2

PDR^*) can penetrate more effectively than the latter, shield themselves from destructive radiation by producing larger quantities of photoprotecting pigments than the algae in eutrophic waters, where less PDR^* can penetrate owing to the strong attenuation of light with depth. The results of the empirical verification of the estimated PPC concentrations C_{PPC} using eqs. (9) and (10) are shown in Figure 2c and in Table 2 (item 3). There is a distinct improvement in the precision of these estimates in comparison with the estimates obtained with the oceanic version of the model (item 2). This applies in particular to the systematic errors, which here are much smaller than in the case of the oceanic model.

3.2. Baltic model formulas for calculating the vertical profiles of photosynthetic pigment (PSP) concentrations

As in the case of the photoprotecting pigments in the Baltic, the first step in the search for model formulas to describe the concentrations of photosynthetic pigments in Baltic phytoplankton (formulas useful in remote sensing algorithms) was to assess the possibility of applying the formulas already defined for oceans. These formulas describe the dependence of the concentrations of these pigments (PSP) on the spectral fitting functions F_j (see eqs. (4)–(6) in the Introduction). The errors of these estimates of Baltic PSP content calculated using the oceanic formulas (see Tables 3A, 3B, 3C – items 2 in these tables) were, however, much greater than the errors of the estimates of empirical data from the oceans (see item 1 in these tables). The oceanic formulas are therefore not suitable for the Baltic. It appears that the chromatic adaptation mechanisms of the photosynthetic apparatus in Baltic phytoplankton are far more complex than those described for oceanic

Table 3. Relative errors in the estimation of the photosynthetic pigment groups (C_{PSC} – table A, C_b – table B, C_c – table C, C_{phyc} – table D) using:

1 – the oceanic version of the model (eqs. (5a)–(5c)) in the oceans (after Majchrowski & Ostrowska (2000))
2 – the oceanic version of the model (eqs. (5a)–(5c)) in the Baltic
3 – the Baltic version of the model (eqs. (11a)–(11b); (12a)–(12b); (13a)–(13b); (14a)–(14b)) in the Baltic

		Arithmetic statistics		Logarithmic statistics			
		systematic error	statistical error	systematic error	standard error factor	statistical error	
Version	Item	$<\varepsilon>$ [%]	σ_ε [%]	$<\varepsilon>_g$ [%]	x	σ_- [%]	σ_+ [%]
A	1	3.96	± 32.0	–0.220	1.32	–24.2	31.9
	2	354	± 387	229	2.336	–57.2	133
	3	19.2	± 76.3	–0.466	1.822	–45.1	82.2
B	1	15.4	± 72.5	–0.0695	1.68	–40.4	67.9
	2	110	± 206	51.2	2.144	–53.1	114
	3	18.6	± 74.8	0.024	1.772	–43.6	77.2
C	1	9.46	± 51.5	–0.0008	1.52	–34.2	52.0
	2	187	± 165	150.5	1.678	–40.4	67.8
	3	11.3	± 59.7	–1.67	1.636	–38.9	63.6
D	3	16.9	± 70.5	0.024	1.740	–42.5	74.0

waters. Setting up a more insightful model of the chromatic adaptation of phytoplankton in the Baltic, one that would be a far more accurate reflection of reality, is not yet possible; this will require further thorough empirical and theoretical studies. That is why, for practical purposes, at the present stage of research, it was attempted to establish other, simpler expressions describing the concentrations of these antenna pigments, based on purely correlational analyses of the empirical material rather than on physical modelling.

After numerous attempts at establishing statistically reliable relationships between the concentrations of photosynthetic accessory pigments and various environmental factors, for practical purposes the formulas given below were accepted; they were established statistically using the methods of multivariate non-linear regression. They are mathematical formulas describing the dependence of the relative accessory pigment contents, i.e., C_b/C_a, C_c/C_a, C_{PSC}/C_a, and also C_{phyc}/C_a on two variables – the trophic index of a basin, given by the surface concentration of chlorophyll a ($C_a(0)$), and the optical depth τ in the sea. It was also found that the estimates obtained were better if the empirical material analysed was divided into two periods: these were named 'winter' (days of the year: 1–118 and 261–365) and 'summer' (days of the year: 119–260). For each of these periods the following formulas were established for a given group of pigments enabling their concentrations to be determined (the variable x in these equations stands for $x = \log(C_a(0))$):

– concentration of chlorophyll b

$$C_b = C_a \times 10^{-1.0703-0.15999\tau+0.046312\tau^2-0.30871x-0.040076x\tau-0.074687x^2} \quad \text{winter} \quad (11a)$$

$$C_b = C_a \times 10^{-0.8808+0.075078\tau-0.023728\tau^2-0.54886x+0.046307x\tau+0.20785x^2} \quad \text{summer} \quad (11b)$$

– concentration of chlorophyll c

$$C_c = C_a \times 10^{-1.2314+0.14836\tau-0.031219\tau^2+0.051019x-0.0093837x\tau+0.053311x^2} \quad \text{winter} \quad (12a)$$

$$C_c = C_a \times 10^{-1.1330+0.1146\tau-0.020600\tau^2-0.011478x+0.0037213x\tau-0.0082814x^2} \quad \text{summer} \quad (12b)$$

– concentration of photosynthetic carotenoids PSC

$$C_{PSC} = C_a \times 10^{-1.1436+0.064027\tau-0.0054346\tau^2+0.29550x-0.0065549x\tau+0.015895x^2} \quad \text{winter} \quad (13a)$$

$$C_{PSC} = C_a \times 10^{-0.82451+0.072685\tau-0.014871\tau^2+0.016015x+0.010256x\tau+0.029283x^2} \quad \text{summer} \quad (13b)$$

– concentration of phycobilin *phyc*

$$C_{phyc} = C_a \times 10^{1.0366-0.15103\tau+0.0280991\tau^2-0.53620x+0.039989x\tau+0.15519x^2} \quad \text{winter} \quad (14a)$$

$$C_{phyc} = C_a \times 10^{1.0855-0.059569\tau+0.0022592\tau^2-0.63758x+0.068297x\tau+0.26215x^2} \quad \text{summer} \quad (14b)$$

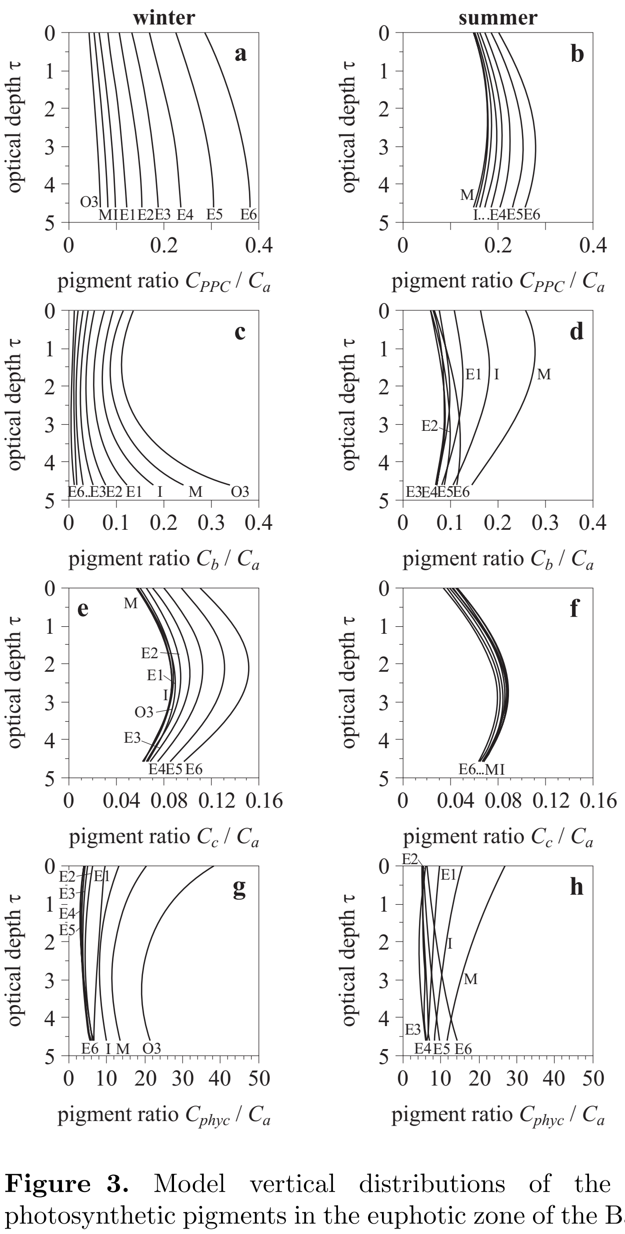

Figure 3. Model vertical distributions of the relative concentrations of photosynthetic pigments in the euphotic zone of the Baltic Sea – depth is expressed in units of optical depth τ; photosynthetic carotenoids, C_{PSC}/C_a, eqs. (13a) and (13b) (a, b); chlorophyll b, C_b/C_a, eqs. (11a) and (11b) (c, d); chlorophyll c, C_c/C_a, eqs. (12a) and (12b) (e, f); phycobilins C_{phyc}/C_a, eqs. (14a)–(14b) (g, f)

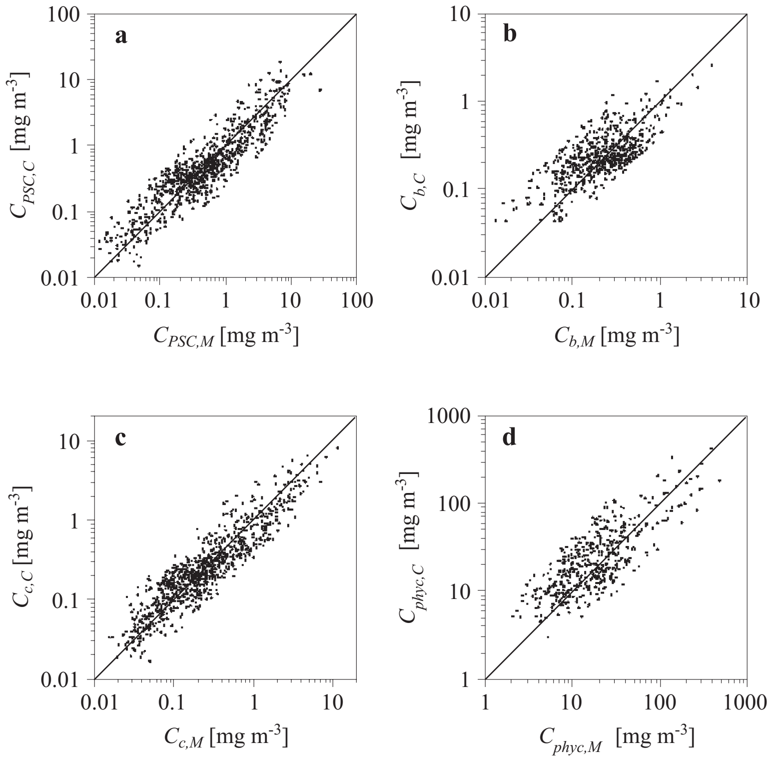

Figure 4. Comparison of empirical (measurement, index M) $C_{PSC,M}$ and modelled (computed, index C) concentrations of pigments: C_{PSC}, formulas (13a) and (13b) (a); C_b, formulas (11a) and (11b) (b); C_c, formulas (12a) and (12b) (c); C_{phyc}, formulas (14a) and (14b) (d) at different stations and depths in the Baltic Sea

Figure 3 illustrates such model concentration depth profiles of the different groups of antenna pigments in Baltic waters of different trophic index, calculated on the basis of these equations. It shows that these profiles are dependent in a highly complex manner on depth in the sea, the trophic index of the waters in question and the season, which is evidence enough for the far greater degree of complexity of the chromatic adaptation processes taking place in Baltic waters than in oceanic waters.

The results of the empirical verification of the concentrations of the different groups of photosynthetic pigments in the Baltic calculated using the above Baltic formulas are illustrated in Figure 4, and the errors in the estimates are given in Tables 3A, B, C, D (items 3). These errors are significantly smaller than those resulting from the application of the oceanic version to the model description of the vertical distributions of antenna pigment concentrations in the Baltic (items 2), where the errors in the estimates of the photosynthetic pigment groups C_j were determined in the same way as those of the photoprotecting carotenoids C_{PPC} (see Table 2).

4. Final remarks

The objective of this work has been achieved. The model expressions worked out here for the surface layer of the sea down to an optical depth of $\tau \approx 5$ (i.e., exceeding the thickness of the euphotic layer) enable the following to be determined:

- concentrations of photoprotecting pigments in Baltic waters relative to the concentration of chlorophyll a, $C_a(\tau)$, $C_{PPC}(\tau)/C_a(\tau)$, at any optical depth in the sea on the basis of the known trophic index of the basin (i.e., $C_a(0)$) and known values of the PAR irradiance just below the sea surface (PAR(0)) (eqs. (9) and (10));
- relative (with respect to the concentration of chlorophyll a, $C_a(z)$) concentrations of photosynthetic pigments in Baltic waters $C_b(\tau)/C_a(\tau)$, $C_c(\tau)/C_a(\tau)$, $C_{PSC}(\tau)/C_a(\tau)$, $C_{phyc}(\tau)/C_a(\tau)$ on the basis of the known trophic index of the basin (i.e., $C_a(0)$) and optical depth τ (eqs. (11)–(14)).

If the model description of the vertical distributions of chlorophyll a concentrations in the sea (see part 1, Ostrowska et al. (2007), this volume) is also taken into account, the formulas presented here will also enable the vertical distributions of the absolute concentrations of all these pigments to be estimated: $C_{PPC}(\tau)$, $C_b(\tau)$, $C_c(\tau)$, $C_{PSC}(\tau)$, $C_{phyc}(\tau)$. At the present stage of research, the precision of these estimates (see the errors listed in Table 3, item 3) can be regarded as satisfactory; in the near future, however, these formulas will be applied in the algorithm for the remote sensing of pigment concentrations and primary production in the Baltic. At the same time, this research will be continued with the aim of obtaining formulas that will guarantee an even better precision of these estimates.

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