

Parameterization of phytoplankton spectral absorption coefficients in the Baltic Sea: general, monthly and two-component variants of approximation formulas

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1. Introduction

If we wish to fully describe the process of photosynthesis in the seas and oceans, and to correctly interpret remote observations of water bodies, it is important to obtain an accurate quantitative description of the spectral characteristics of light absorption by living phytoplankton, a significant constituent of seawater (see e.g. Kirk 1994, Mobley 1994, or Woźniak and Dera 2007). The efficiency of sunlight absorption by this phytoplankton generally depends on a number of factors. The principal, strongly absorbing components of phytoplankton are the pigments it contains: chlorophyll *a*, the basic photosynthetic pigment, and accessory – photosynthetic and/or photoprotective – pigments. Light absorption by phytoplankton thus depends primarily on the properties and concentrations of these several pigments. It is known *inter alia* from theoretical considerations that the very structure, dimensions and shapes of individual phytoplankton cells can also influence the efficiency with which their populations absorb sunlight. It is important to know by what means and how densely the strongly light-absorbing pigments are "packed" within the internal structures of such cells (see e.g. Morel and Bricaud 1981, 1986). Given the complexity of all these relationships, it is often necessary (or even required) for practical purposes to take a highly simplified approach. It is a common simplification to assume that all the relevant properties of a phytoplankton population can be roughly parameterized using just one variable – the concentration of chlorophyll *a*. The papers by Bricaud et al. (1995, 1998), often cited by other authors, were among the first to introduce approximate description of the light absorption vs chlorophyll *a* concentration relationship. They proposed using a power function to account for the general decrease in light absorption efficiency per unit chlorophyll *a* concentration that occurs with increasing absolute values of this concentration in seawater. The papers by Bricaud et al. (1995, 1998) were based on extensive empirical material gathered in different regions of open, oceanic waters, classified as 'case 1 waters'. In many later works different authors addressed the similar problem. Examples of spectral power function parameterizations for different marine environments can be found in Stramska et al. (2003), Staehr and Markager (2004), Matsuoka et al. (2007), Dmitriev et al. (2009), Nima et al. (2016), Churilova et al. (2017) and Mascarenhas et al. (2018) to name only a few.

The Baltic Sea, the region we have been studied, is a semi-enclosed, brackish sea basin classified as an example of 'case 2 waters'. It is characterized by usually high concentrations of dissolved organic substances of terrestrial origin (see e.g. Kowalczyk 1999). In regards to living phytoplankton its biomass and species composition in the Baltic is known to vary during the year. Usually there are three main phytoplankton blooms: a spring bloom of cryophilous diatoms, which transforms into a bloom of dinoflagellates (early March - May); a summer bloom of cyanobacteria (July and August); and an autumn bloom of thermophilous diatoms (September - October) (see Wasmund et al. 1996 and 2001, Witek and Pliński 1998, Wasmund and Uhlig, 2003 and Thamm et al. 2004).

The are two objectives/aims of this work:

- the main objective is to find new forms of classic power function parameterizations for the phytoplankton absorption coefficient adapted to the specific conditions of the Baltic Sea. An important aspect of this is to document how large are the differences between the coefficients of spectral parameterization when they are matched separately for data from selected periods of the year.
- an additional aim of this work is to propose a modified, but still relatively simple form of parameterization, that would allow to take into account the diversity of phytoplankton absorption properties observed during the year in the studied area.

The new forms of parameterization that we are seeking can be used, among other things, to develop and improve the accuracy of practical, local algorithms for interpreting remote observations of the Baltic Sea.

2. Materials and methods

The empirical data used in this study were collected at more than 170 measuring stations in various parts of the southern and central Baltic Sea, though mainly in the Polish economic zone, from 2006 to 2014 (see Figure 1). These data were acquired principally during 42 short research cruises on board r/v Oceania at different times of the year.

During the research cruises a diversity of physical and optical parameters of seawater were measured *in situ* at each sampling station. Discrete seawater samples for further laboratory analysis were also collected. This work analyses certain optical properties (spectra of coefficients of light absorption by phytoplankton) and biogeochemical properties (concentrations of chlorophyll *a* and other phytoplankton pigments) only of discrete surface seawater samples.

In order to determine the spectra of phytoplankton absorption coefficient a_{ph} , we measured the spectra of absorption coefficients for all suspended particles retained on filters (a_p), and also, after chemical bleaching of pigments in our samples (2% solution $\text{Ca}(\text{ClO})_2$ (Koblentz-Mishke et al. 1995, Woźniak et al. 1999)), the corresponding spectra of non-algal particles (a_{NAP}). Optical measurements were performed in the 350-750 nm spectral range with a UNICAM UV4-100 double-beam spectrophotometer equipped with an integrating sphere of external diameter 66 mm (LABSPHERE RSA-UC-40). For the reference measurements we used clean filters rinsed with particle-free seawater. The methodology of combined light-transmission and light-reflection measurements (called T-R method) described by Tassan and Ferrari (1995, 2002) was applied. From combined results of these measurements, it was possible to calculate the optical density of each sample collected on filter, $OD_s(\lambda)$. To calculate absorption coefficients of particles in solution, appropriate correction has to be made to compensate for the elongation of the optical path of the light due to the multiple scattering occurring in the material collected on the filter. This is done by applying the dimensionless path length amplification, the β -factor proposed by Stramski et al. (2015) for the T-R method:

$$OD_{\text{sus}}(\lambda) = 0.719OD_s(\lambda)^{1.2287}. \quad (1)$$

The coefficient of light absorption by all suspended particles was then calculated using the formula:

$$a_p(\lambda) = [\ln(10) \cdot OD_{\text{sus}}(\lambda)]/l, \quad (2)$$

where l [m] is the hypothetical optical path in solution, determined as the ratio of the volume of filtered water to the effective area of the filter. The absorption by non-algal particles $a_{NAP}(\lambda)$

were determined in an analogous way. Finally the sought-after a_{ph} coefficient can be calculated as a difference between a_p and a_{NAP} .

HPLC was used to determine phytoplankton pigment concentrations; the methodology is described in detail in Stoń and Kosakowska (2002) and Stoń-Egiert and Kosakowska (2005). In this work we refer mainly to the total chlorophyll *a* concentration (*Tchla*) (defined as the sum of chlorophyll *a*, allomer and epimer, chlorophyllide *a* and phaeophytin *a*), and to the sum of the concentrations of all accessory pigments ΣC_i , i.e. the sum of chlorophylls *b* (*Tchl**b*), chlorophylls *c* (*Tchl**c*), photosynthetic carotenoids (*PSC*) and photoprotective carotenoids (*PPC*).

3. Results and discussion

3.1. General characteristics of the data

Figure 2 shows chosen examples of a_{ph} coefficient spectra that we recorded in the Baltic Sea. These spectra exhibit the expected characteristic absorption maxima in both the blue (ca 440 nm) and red (ca 675 nm) bands. The variability of $a_{ph}(\lambda)$ was almost three orders of magnitude. For blue light, for example, $a_{ph}(440)$ varied from 0.014 m⁻¹ to 3.85 m⁻¹, whereas for the local absorption maximum in the red band, $a_{ph}(675)$ varied from 0.006 m⁻¹ to 1.74 m⁻¹.

Figure 3 illustrates the ranges of variability of *Tchla* and ΣC_i as well as their ratio for all the pooled data and for individual sampling periods (months). This shows that with respect to all the data analysed, the ranges of variability of both *Tchla* and ΣC_i are, like the absorption coefficient, almost three orders of magnitude (0.41-141.8 mg m⁻³ and 0.15-72.1 mg m⁻³ respectively). The average *Tchla* for all the data was 7.69 mg m⁻³. In the spring and summer months mean *Tchla* concentrations were above average, while in autumn and winter were lower. In general, a similar trend of average changes in individual months emerges from an analysis of the sum of accessory pigment concentrations ΣC_i . Taking into account all the data from different periods of the year, we can say that measured values of ΣC_i correlate fairly well with *Tchla* (Figure 3c). Nevertheless, if we look at the $\Sigma C_i/Tchla$ ratio, we see that its average values also changed significantly during the year (Figure 3b). The average value of $\Sigma C_i/Tchla$ for all the data was 0.66, but the full range of variability that we recorded was from 0.21 to 1.5. For the months of April, May and September, the average $\Sigma C_i/Tchla$ was higher than or equal to the average for the whole year (0.66, 0.79 and 0.69, respectively). In the remaining months, the averages were lower than the general average – from 0.50 to 0.61. This latter fact is a clear indicator of the obvious limitations of applying solely the chlorophyll *a* concentration as a simplified measure to describe the overall pigment population, and to which measure the light absorption of pigments is customarily parameterized.

3.2. Approximate description of the light absorption coefficient by phytoplankton

3.2.1. General and monthly variants of one-component parameterizations

We carried out statistical analyses of our measurement data in order to define classic forms of the approximate functional relations between the coefficient $a_{ph}(\lambda)$ and the concentration *Tchla*. Like Bricaud et al. (1995, 1998), we approximated these relations using power functions:

$$a_{ph}(\lambda) = A(\lambda) \cdot Tchla^{E(\lambda)}. \quad (3)$$

Note that coefficient $A(\lambda)$ determined in this way reflects the numerical value of the absorption coefficient $a_{ph}(\lambda)$ which the approximated relationship assigns to the case when the *Tchla* is exactly 1 mg m⁻³. The coefficient $E(\lambda)$ of equation (3) is a dimensionless quantity, which is the exponent of the power to which the chlorophyll *a* concentration is raised.

The coefficients of the approximate formula (3) were determined over the entire available spectral range from 350 to 700 nm with a resolution of 1 nm. Figure 4a,b and c presents different variants of the spectra of coefficients $A(\lambda)$ and $E(\lambda)$, along with the respective values of R^2 . These variants represent parameterizations based on all available data (a general variant) as well as alternative parameterizations derived for data subsets relating to particular months (monthly variants). Analysis of the curves in Figure 4a and b shows that the coefficients of the monthly parameterizations differ, exhibiting larger or smaller deviations from the course of the general variant's coefficients. In the case of coefficient A , the differences between 350-590 nm and around 675 nm are particularly conspicuous. As regards coefficient E , the differences between the alternative parameterizations occur over the entire spectral range. In the case of the general variant, E changes only slightly, between 0.81 and 0.91. In contrast, the values of E for the parameterizations derived for individual months are spectrally more differentiated, with more pronounced local maxima and minima.

3.2.2. Two-component parameterization

As already indicated in section 3.1, there is noticeable variation in the proportion between *Tchla* and the concentrations of other phytoplankton pigments in particular months of the year within our dataset (Figure 3). This variability initially indicated the limitations that may crop up when using the chlorophyll *a* concentration as the only variable for parameterizing the spectra of $a_{ph}(\lambda)$. Such limitations became visible, when we documented the differences between the parameterizations matched up to the data from selected months. As a step towards improving the accuracy of a_{ph} coefficient parameterization, while retaining the relative simplicity of the mathematical formalism used, we found that the best for this particular purpose is the ratio of all accessory pigments to chlorophyll *a* ($\Sigma C_i/Tchla$). The new expression that approximates $a_{ph}(\lambda)$ by treating it as a function of two variables may be as follows:

$$a_{ph}(\lambda) = A_0(\lambda) \cdot e^{K(\lambda) \frac{\Sigma C_i}{Tchla}} \cdot Tchla^{E(\lambda)}, \quad (4)$$

where $A_0(\lambda)$ [$m^2 mg^{-1}$], and $K(\lambda)$ [no units]. Note that coefficient $E(\lambda)$ [no units] takes the same values as those in the general variant of the one-component parameterization. Note, too, that the product of the new coefficient $A_0(\lambda)$ and the exponential function appearing in equation (4) allows one, with the adopted value of the ratio $\Sigma C_i/Tchla$, to calculate the value corresponding to coefficient $A(\lambda)$ from the parameterization given by formula (3). We define this product as:

$$A' \left(\lambda, \frac{\Sigma C_i}{Tchla} \right) = A_0(\lambda) \cdot e^{K(\lambda) \frac{\Sigma C_i}{Tchla}}. \quad (5)$$

Spectral values of the new coefficients of equation (4) (coefficients $A_0(\lambda)$ and $K(\lambda)$) are shown in Figure 5.a, and Figure 5.b illustrates the family of $A'(\lambda, \Sigma C_i/Tchla)$ curves plotted for selected values of $\Sigma C_i/Tchla$ in our database.

3.3. Estimation errors of different variants of parameterizations

We performed an extensive analysis of errors made using different variants of the proposed approximation formulas. Different cases were considered: the formulas were tested on the whole dataset as well as on data from particular months only. In our analyses we used both the arithmetic statistics of relative errors and also the so-called logarithmic statistics, as these are generally appropriate when the variation of tested/estimated quantities span several orders of magnitude.

Table 1 contains statistics of estimation errors when different variants of parameterizations were tested on the whole dataset. Three scenarios are considered: first, when the general variant of the parameterization was used to calculate absorption coefficients; second, when the relevant variants of monthly parameterizations were used, depending on the

month of data acquisition; and third, when the two-component parameterization was used (the values for the second and third scenarios are given in parentheses). All these results are presented at selected light wavelengths chosen to cover the spectral range under consideration and include the characteristic maxima of light absorption by chlorophyll *a*. We found that the errors of estimation of coefficients a_{ph} obtained using the general parameterization are relatively stable across the range from 400 to 690 nm. Because the general parameterization was developed using linear least-squares regression applied to the logarithms of $Tchl_a$ and a_{ph} values, the systematic error according to logarithmic statistics is always equal or very close to zero. The standard error factor (showing how many times the value approximated by a given formula differs from the empirical one), varies between 1.37 and 1.52 for wavelengths from 400 to 690 nm. This means that the statistical error according to logarithmic statistics in the 400-690 nm range varies from -34% to 52%. For the second scenario of calculations done over the entire dataset, i.e. when different monthly parameterization were used on an entire dataset, the errors are only slightly lower than the previous ones. Applying logarithmic statistics to this scenario leads to a standard error factor varying from 1.34 to 1.49 in the 400-690 nm range. Hence, the statistical error according to logarithmic statistics in the 400-690 nm range varies from -33% to 49. In the third scenario, i.e. when the new two-component parameterization was applied to a whole dataset, we found estimation errors to lay generally between errors of scenarios first and second. In terms of logarithmic statistics the standard error factor in the range between 400 and 690 nm varies from 1.35 to 1.52. A detailed comparison of the results obtained indicates that the use of the two-component parameterization on a whole dataset leads to a small but noticeable reduction in the errors compared with use of the general version of the one-component parameterization (eq. 3) only in the 390-530 nm and 665-685 nm spectral ranges. These are the ranges in which significant differences in the family of $A'(\lambda, \Sigma C_i / Tchl_a)$ curves have been observed (see Figure 5). However, comparison of the estimation errors associated with the two-component parameterization with the scenario of using monthly variants of the one-component parameterization slightly favours the latter.

The estimation errors mentioned above were calculated over the entire available dataset. We also tested how much more accurate the results might be if different variants of parameterization were tested on data only from one particular month (detailed results are not presented here for brevity). We generally found that using the monthly parameterization instead of a general variant for individual months has often little reduction effect on the level of statistical error, although it may have, a significant impact by the strong reduction of systematic error. In regards to two-component parameterization, we found that applying it instead of general variant of one-component parameterization, usually allows to reduce the statistical errors in the vicinity of phytoplankton absorption peaks. In terms of systematic error a reduction was observed only in some of the months analysed.

3.4. Comparison with selected examples of parameterizations from the literature

We shall briefly compare our results with other examples of parameterizations from the literature. In additional two panels of Figure 5 (panels d and e) we plotted coefficients of parameterization obtained by Bricaud et al. (1995), Stramska et al. (2003), Matsuoka et al. (2007), Nima et al. (2016) and Churilova et al. (2017). These examples were chosen from among many known in the literature, in order to illustrate the possible variability occurring between coefficients of different parameterizations that were originally matched to different datasets. In the case of coefficients A , all spectral shapes presented in Figure 5d generally reflect the characteristic absorption maxima in the blue and red spectral ranges. Quantitatively, however, there are significant differences between these examples, the largest being in the wavelength range from about 400 to 480 nm. Interestingly, such a range of A coefficient variability looks similar as the one we obtained with our own Baltic data by developing separate

variants of the one-component parameterization for individual months (compare Figure 5a). With regard to the values of coefficients E , the literature examples presented in Figure 5e significantly differ from each other and all exhibit a distinct variation of values across the spectrum. According to literature sources chosen for presentation, coefficients E can take values from under 0.5 to even more than 1 in different spectral ranges. In our analyses we also found spectral variation of E values, but only for parameterization variants that were matched to the data from separate months; when all our data were pulled together the resulting E coefficient spectral shape was relatively flat (with values between 0.8 and 0.9 for general variant of parameterization; compare Figure 5b).

4. Final remarks

New variants of the parameterization of coefficient a_{ph} in Baltic Sea were developed. They should be treated as simplified and practical relationships of a local character, tailored to the specifics of the target environment. The new empirical formulas include classic one-component parameterizations, where the only variable is the concentration of chlorophyll a . Parameterizations of this type have been developed both as a general version, i.e. one matched to all data collected in different periods of the year, and in the form of separate variants adjusted to the individual months of data collection. Importantly, we found that the coefficients of monthly variants could differ from each other very significantly, thus indirectly reflecting the annual variation in the proportions between chlorophyll a and other photosynthetic or photoprotective pigments. We also presents a new form of parameterization that uses one additional variable: the ratio of the concentrations of accessory pigments to the concentration of chlorophyll a . With all the variants of this parameterization, spectra of coefficient a_{ph} can be estimated fairly simply, and with few requirements as to input data. Such estimates can be made over a wide spectral range (from 350 to 700 nm) and with a high spectral resolution (1 nm). Their estimation accuracy, although limited (see Table 1), appears satisfactory, since the real values of a_{ph} vary in Baltic Sea conditions almost three orders of magnitude. Our study has also shown that further improvement in the accuracy of the approximate description of a_{ph} spectra is possible, at least in some applications. In case of datasets from different times of the year such improvement can be achieved by using 'dynamically selected' monthly variants of parameterizations, or, when the data on pigments composition are available, by using the new two-component parameterization. In case of data subsets limited to individual months, especially the use of appropriately selected monthly variants may allow to avoid the occurrence of significant systematic errors. Another important qualitative observation from our analyses is that new variants of monthly parameterizations have a range of variability of coefficients similar to that between different literature parameterizations established on the basis of data from various aquatic environments. This particular observation reminds us that all such parameterizations are always quite far-reaching simplifications of relationships occurring in nature. The variability of these relationships that we recorded throughout the year in the Baltic Sea seems to indicate that only the use of a much more elaborate mathematical apparatus, using a much larger number of variables describing the composition of pigments and other features of the phytoplankton population, could further and more radically improve the accuracy of the spectral description of the light absorption coefficient (see, e.g., the multi-component models presented in Woźniak et al. 1999, Woźniak et al. 2000 a and b, Majchrowski et al. 2000, Ficek et al. 2004). In our opinion, however, the practical value of the simple parameterizations presented in this work should be seen in the opportunities for applying them to the development of various methods and algorithms, whose specificity from the very beginning requires the use of simplifications.

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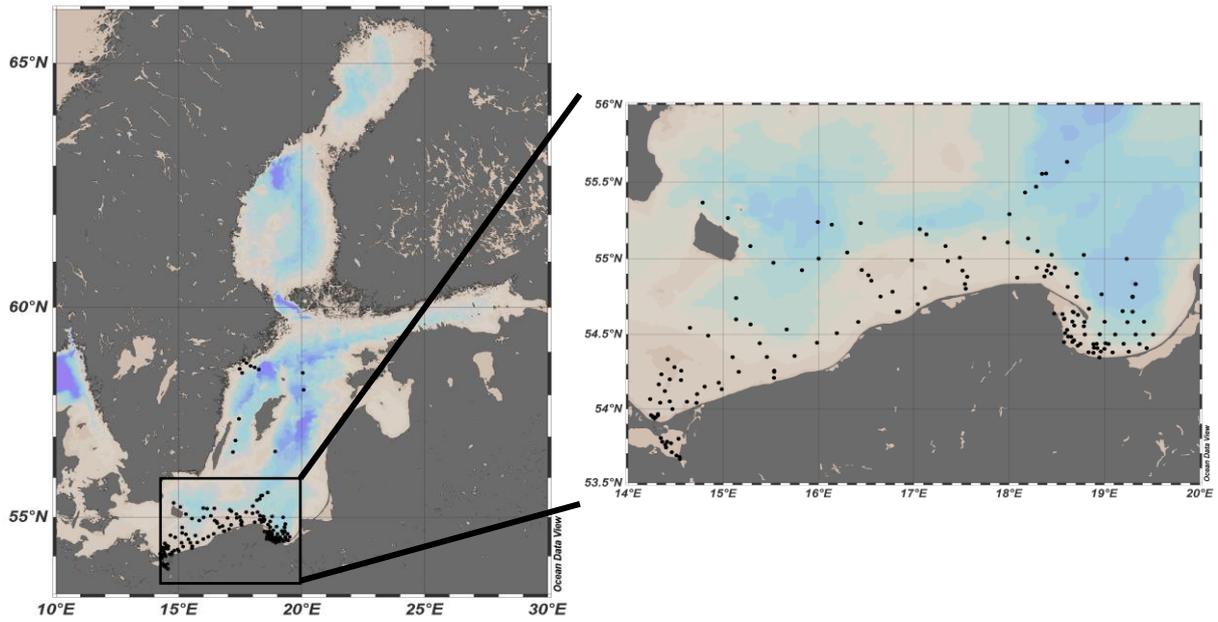


Figure 1. Locations of all sampling stations in the Baltic Sea.

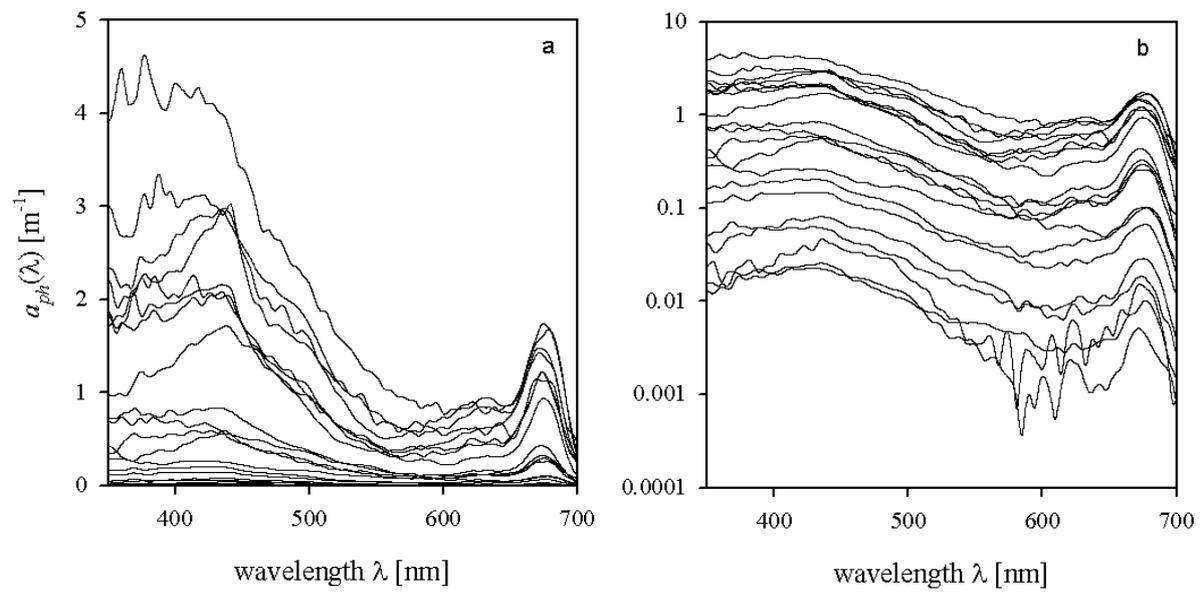


Figure 2. Examples of spectra of the light absorption coefficient $a_{ph}(\lambda)$ representing the variability range of the data analysed in the present paper.

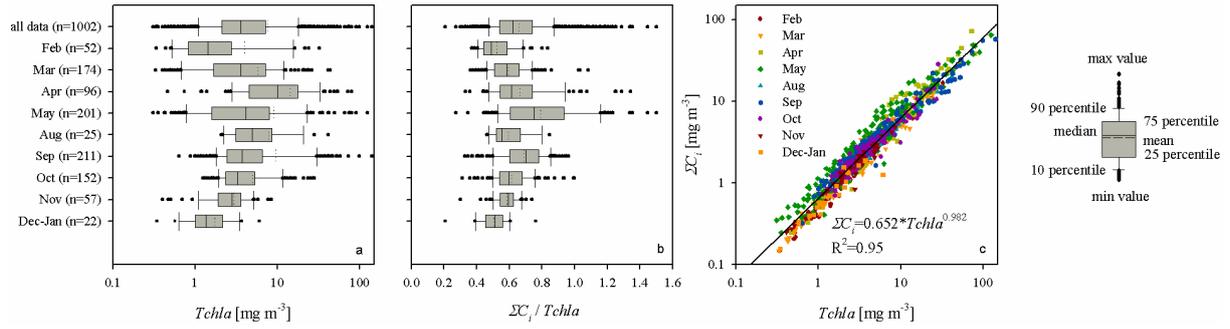


Figure 3. Ranges of variability of $Tchla$ concentration (a) and the ratio $\Sigma C_i / Tchla$ (b) for all the data analysed and for each sampling month; (c) the relationship between ΣC_i and $Tchla$.

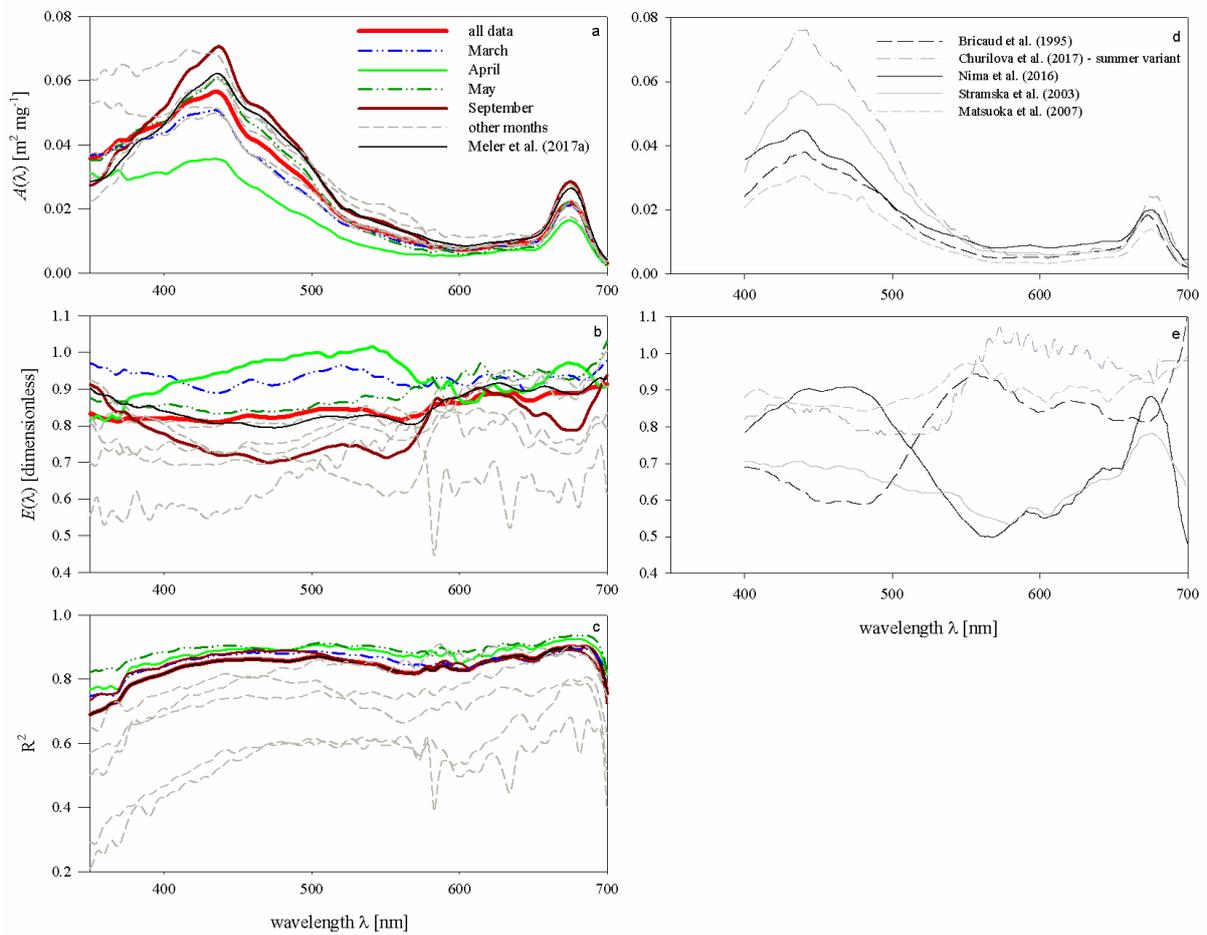


Figure 4. Coefficients A (a) and E (b) of the parameterizations given by Eq.(1), and the corresponding values of the determination coefficient R^2 (c), determined for all analyzed data and for each sampling month. Examples of coefficients A (d) and E (e) given by various authors.

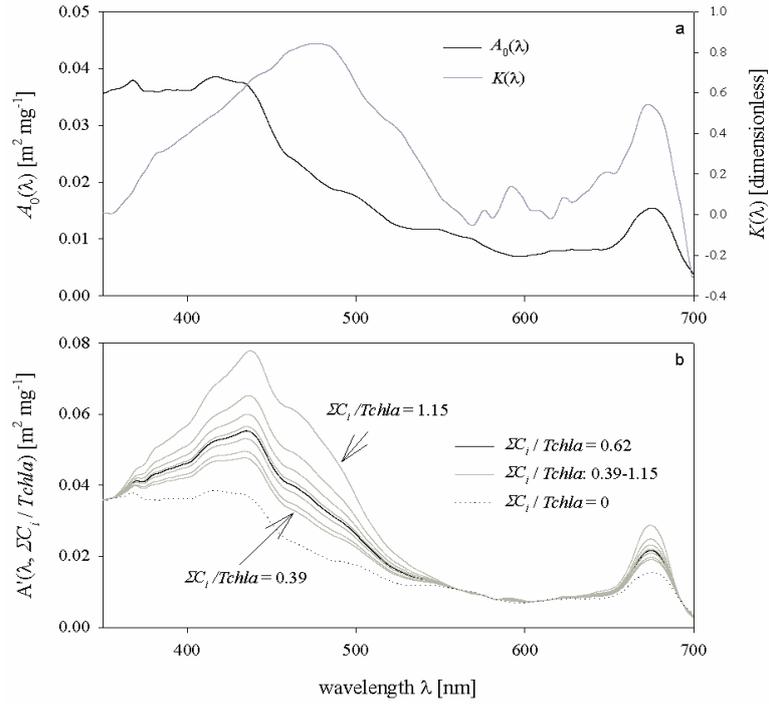


Figure 5. (a) Coefficients A_0 and K of the two-component parameterization given by Eq.(2); (b) examples of curves representing coefficient $A'(\lambda, \Sigma C_i / Tchl a) = A_0(\lambda) \exp[K(\lambda) * \Sigma C_i / Tchl a]$, for the selected value of the ratio $\Sigma C_i / Tchl a$.

Table 1. Statistics of estimation errors* of coefficient $a_{ph}(\lambda)$ when the different variants of parameterization were applied to the entire dataset (n= 1002). The calculated values are given for three scenarios: when the general variant of one-component parameterization was used; when variants specific to individual months were chosen; and when two-component parameterization was used.

λ [nm]	Arithmetic statistics of relative error			Logarithmic statistics		
	systematic error $\langle \varepsilon \rangle [\%]$	statistical error $\sigma_\varepsilon [\%]$	systematic error $\langle \varepsilon \rangle_g [\%]$	standard error factor x	statistical error $\sigma_+ [\%]$ $\sigma_- [\%]$	
400	8.5 (7.7; 8.1)	45 (42; 43)	0 (-0.01; -0.14)	1.51 (1.48; 1.51)	51 (48; 51)	-34 (-33; -34)
440	6.3 (5.2; 5.4)	39 (34; 35)	0 (-0.01; -0.13)	1.42 (1.38; 1.40)	42 (38; 40)	-30 (-28; -28)
500	6.1 (5.2; 5.2)	37 (34; 34)	0 (-0.04; -0.17)	1.42 (1.38; 1.39)	42 (38; 40)	-29 (-28; -28)
550	7.6 (6.7; 7.6)	42 (39; 43)	0 (-0.05; -0.13)	1.47 (1.44; 1.48)	48 (44; 48)	-32 (-31; -33)
600	8.8 (8.1; 8.8)	47 (46; 48)	0 (-0.15; -0.10)	1.52 (1.49; 1.52)	52 (49; 52)	-34 (-33; -34)
675	5.0 (4.2; 4.4)	34 (31; 32)	0 (-0.04; -0.15)	1.37 (1.34; 1.35)	37 (34; 36)	-27 (-25; -26)
690	5.8 (5.4; 5.8)	37 (37; 38)	0 (-0.11; -0.15)	1.40 (1.39; 1.41)	40 (39; 41)	-29 (-28; -29)

***) The arithmetic statistics of relative error:**

- mean of relative error (representing the systematic error according to arithmetic statistics):

$$\langle \varepsilon \rangle = N^{-1} \sum_{i=1}^N \varepsilon_i, \text{ where } \varepsilon = \frac{(P_i - O_i)}{O_i}, O_i - \text{observed/measured values, } P_i - \text{predicted/estimated values}$$

- the standard deviation of relative error (representing the statistical error according to arithmetic statistics):

$$\sigma_\varepsilon = \sqrt{\frac{1}{N} (\sum_{i=1}^N (\varepsilon_i - \langle \varepsilon \rangle)^2)}$$

The logarithmic statistics:

- the mean logarithmic error (representing the systematic error according to logarithmic statistics):

$$\langle \varepsilon \rangle_g = 10^{\langle \log(\frac{P_i}{O_i}) \rangle} - 1, \text{ where } \langle \log(\frac{P_i}{O_i}) \rangle \text{ is the mean of } \log(\frac{P_i}{O_i})$$

- the standard error factor (the quantity which allows one to calculate the range of statistical errors according to logarithmic statistics):

$$x = 10^{\sigma_{\log}}, \text{ where } \sigma_{\log} \text{ is the standard deviation of the set } \log(\frac{P_i}{O_i})$$

- statistical logarithmic errors (representing the range of statistical errors according to logarithmic statistics):

$$\sigma_- = \frac{1}{x} - 1, \quad \sigma_+ = x - 1$$