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## МОДЕЛИРОВАНИЕ КОЭФФИЦИЕНТОВ ПОГЛОЩЕНИЯ СВЕТА ФИТОПЛАНКТОНОМ В ОЗЕРАХ ПОМЕРАНИИ (СЕВЕРНАЯ ПОЛЬША)

В 2004–2008 гг. поглощательные характеристики фитопланктона были измерены в 15 озерах северной Польши различной продуктивности одновременно с концентрацией оптически активных веществ. Эти данные были использованы для проверки модели поглощательных свойств фитопланктона, предложенной Брико и др. для океанских вод типа 1 (в дальнейшем называемой параметризацией Брико) для предсказания спектров поглощения света фитопланктоном  $a_{ph}$  в озерах Померании. Данное исследование показывает ограничения этой модели для озерного фитопланктона, и обсуждаются их причины. Кроме того, предлагается на том же математическом базисе, что и модель Брико, но при других значениях соответствующих эмпирических параметров, аналогичная модель поглощения света фитопланктоном в исследованных озерах. Для простоты анализируются коэффициенты поглощения только в поверхностных водах. Результаты анализа сравниваются с результатами других авторов, полученных для вод типа 1 с использованием аналогичных моделей.

**Ключевые слова:** спектры поглощения фитопланктона, озера, био-оптическое моделирование.

Modelling the optical properties of phytoplankton, in particular their absorption properties, is a subject of study in many scientific centres. Such modelling we understand the attempts to derive mathematical expressions for calculating the coefficient of light absorption by phytoplankton on the basis of known concentrations of chlorophyll  $a$  or of other pigments, and possibly other environmental parameters. A range of light absorption models derived for oceanic waters (case 1 waters) is reported in the subject literature [1, 2–5]. But attempts to apply these models to lake waters (case 2 waters), which usually contain very large concentrations of various optically active constituents (OACs), have not yielded very satisfactory results. No one has come up with a universal model for light absorption that would allow this magnitude to be determined in lake waters with satisfactory precision.

One of the best known and widely applied of such models, in which the coefficient of light absorption by phytoplankton is made dependent on one parameter, i.e. the concentration of chlorophyll  $a$ , is the parameterisation derived by Bricaud et al. [1]. On the assumption that the chlorophyll specific absorption coefficients  $a_{ph}^*$  are strongly dependent on trophicity as determined by the chlorophyll  $a$  concentration, Bricaud et al. accepted the following form of the dependence of these coefficients for various wavelengths on the chlorophyll concentration:

$$a_{ph}^*(\lambda) = A(\lambda) C_a^{-B(\lambda)}, \quad (1)$$

where  $C_a$  – concentration of chlorophyll  $a$ , [ $\text{mg m}^{-3}$ ];  $A$ ,  $B$  – wavelength-dependent parameters, defined by the statistical analysis of oceanic spectra (case 1 waters) (see table 2 in [1]).

Bricaud's parameterisation was based the statistical analysis of phytoplankton absorption data gathered in oceanic areas with  $C_a$  ranging from 0.01 to 25  $\text{mg m}^{-3}$ . Only a tiny fraction of these data refers to waters with  $C_a > 10 \text{ mg m}^{-3}$  such as are found in lakes. This parameterisation takes account of the fact that specific absorption coefficients  $a_{ph}^*$  decrease with rising values of  $C_a$ . The greatest variation in this coefficient is characteristic of oligotrophic waters, in

which the value of  $a_{ph}^*(\lambda)$  declines steeply with increasing  $C_a$ . But in the case of eutrophic waters,  $a_{ph}^*(\lambda)$  varies within only a small range (see fig.1 in [1]). In lakes, chlorophyll concentrations are usually large, exceeding by one or more orders of magnitude those found in marine waters, i.e. those for which Bricaud et al. derived their parameterisation. Even so, the simplicity of this model and the lack of any alternative have persuaded many scientists to apply it to waters in which  $C_a$  is in excess of  $25 \text{ mg m}^{-3}$  (see, for example [6–11]).

The initial objective of the present work was to analyse the possibilities of applying Bricaud's parameterisation to estimate of  $a_{ph}^*$  in a number of lakes in Pomerania (Poland). But as we found that this model has only limited applicability to the lakes in question. A second, more important, objective was also pursued, namely, to derive a similar model of light absorption by phytoplankton, i.e. based on the same mathematical form of equation (1), only with different values of the empirical parameters  $A$  and  $B$ , appropriate to the lakes under investigation. To simplify the problem, the analysis was limited to the absorption coefficients of phytoplankton inhabiting only the surface layers of the lakes.

**Material and methods.** Between 2004 and 2008 we measured the light absorption properties of phytoplankton in 15 lakes of different trophicity in northern Poland. At station representative of the open waters of each lake water samples were collected for analysis usually once a month, except when the lakes were covered with ice. For each station, water samples were filtered for the determination of phytoplankton pigments and light absorption spectra. Concentrations of chlorophyll  $a$  and phaeophytin  $a$  were determined spectrophotometrically after extraction in acetone or ethanol according to the methods of Jeffrey et al. [10], Jeffrey and Humphrey [11]. For the sake of simplicity, the sum of the concentrations of chlorophyll  $a$  and phaeophytin will hereafter be covered by the term 'chlorophyll  $a$  concentration' –  $C_a$  ( $\text{mg m}^{-3}$ ).

The spectra of light absorption by the suspended particulate matter (SPM) in the lake water samples were measured for wavelengths from 350 to 750 nm using a UNICAM UV4-100 spectrophotometer equipped with an integrating sphere (66 mm diameter). The methodology of this Transmission-Reflectance (T-R) filter-pad technique is described in Tassan and Ferrari [12, 13]. The samples were passed through Whatman GF/F filters ( $\phi = 22 \text{ mm}$ ). The volumes of filtered water ranged from 0.01 to 0.5 l and were selected such that the layer of suspended matter collected by the filter had an optical density ( $OD$ ) no greater than 0.5 after subtraction of the filter's own  $OD$ . After filtration the samples were frozen in liquid nitrogen. Immediately prior to the measurements the filters were defrosted and the measurements were made in transmittance and reflectance mode. For a given sample, this technique requires optical density spectra to be measured with at least four different filter-detector configurations involving sample and blank filters. The optical density  $OD_f$  of the particles collected on the filter was calculated from these measurements (see [12, 13]). In order to determine the light absorption by non pigmented material (commonly referred to as detritus) the sample was bleached and the above measurements were repeated. The samples were bleached by saturating them with a 2 % solution of  $\text{CaClO}$ . The bleaching time ranged from 1 to 15 minutes. A problem that crops up with this type of measurement is that the optical path of the light in the sediment samples on the filter is amplified. To eliminate this effect, the optical path length amplification factor  $\beta$ , defined as the ratio of the optical path to the geometrical path in the sample, is introduced into the calculation of the real absorption coefficients of the suspended matter [14]. In practice, the application of this factor involved determining the real optical density of the suspension in water ( $OD_{\text{sus}}$ ) from the optical density obtained from measurements made on the filter ( $OD_f$ ). Experiments carried out by many authors have shown that the dependence of  $OD_{\text{sus}}$  on  $OD_f$  is non-linear and can be described approximately by the equation  $OD_{\text{sus}}(\lambda) = a [OD_f(\lambda)]^2 + b OD_f(\lambda)$  with empirically determined coefficients  $a = 0.592$  and  $b = 0.4$ . This formula is based on experiments with several phytoplankton cultures, mineral-rich particulate assemblages and natural assemblages of particles from marine environments (see [15, 16]). Once the optical densities of the seston  $OD_{\text{sus,ses}}(\lambda)$  and the non pigmented detrital material  $OD_{\text{sus,det}}(\lambda)$  had been

calculated, the values of the corresponding coefficients of absorption  $a_{\text{ses}}(\lambda)$  and  $a_{\text{det}}(\lambda)$  could be derived from them. The spectra of the coefficient of absorption by phytoplankton pigments  $a_{\text{ph}}(\lambda)$  was calculated as the difference  $a_{\text{ph}}(\lambda) = a_{\text{ses}}(\lambda) - a_{\text{det}}(\lambda)$ . In view of the fact that phytoplankton pigments do not absorb near-IR radiation, the non-zero value of  $a_{\text{ph}}(750)$  obtained during the measurements was treated as a measurement error. The entire absorption spectrum  $a_{\text{ph}}(\lambda)$  was corrected by the value of this error on the assumption that this was independent of wavelength.

438 empirical spectra of light absorption  $a_{\text{ph}}(\lambda)$  by phytoplankton were available for analysis. In view of the considerably variability of the absorption spectra at greater depths, however, the analysis was restricted to the surface water layer. The number of spectra was thus reduced to 214.

In addition to the experimental work described here, three further parameters were examined, namely, the SPM concentration  $C_{\text{SPM}}$ , the POM (particulate organic matter) concentration  $C_{\text{POM}}$  and the spectra of the coefficient of light absorption by CDOM (chromophoric dissolved organic matter) contained in the waters of the lakes we studied. The parameters were not analysed in detail in this work, but were used to characterise OACs in the lakes.

The SPM concentration  $C_{\text{SPM}}$  was determined as the difference in mass of GF/F filters before and after filtration. We used specially prepared GF/F filters (diameter 47mm) pre-combusted for 0.5 h at 550°C, pre-washed with doubly distilled water, then dried and pre-weighed. Having been analysed for SPM concentration, the filters were combusted for 0.5 h at 550°C to remove the organic particle fraction, then reweighed. The difference in weight before and after combustion yielded the concentration of POM. Weighing was accurate to 0.01mg.

Absorption by CDOM was measured on a Hitachi U 2810 spectrophotometer. The samples were first passed through Whatman GF/F filters, then through membrane filters with a pore size of 0.2  $\mu\text{m}$ . CDOM samples were refrigerated immediately upon filtration for more than one week before processing. Absorbance was measured in 5 or 10 cm quartz cuvettes with respect to doubly distilled water every 1 nm from 200 to 750 nm. The absorption coefficients  $a_{\text{CDOM}}(\lambda)$  ( $\text{m}^{-1}$ ) were calculated for every wavelength ( $\lambda$ ) according to the formula suggested by Kirk [17]:

$$a_{\text{CDOM}}(\lambda) = 2.303 A(\lambda)/l,$$

where  $A(\lambda)$  is the absorbance measured for a given wavelength, and  $l$  is the length of the cuvette in metres.

**Results and discussion.** For this experiment we chose a series of lakes that would best reflect the great variety of inland waters in this part of Europe. Table 1 lists the range of variation of the OACs. The waters in these lakes contained large quantities of SPM and dissolved matter. Some of the measurements were made in very turbid waters with  $C_a > 300 \text{ mg m}^{-3}$  and  $C_s > 170 \text{ g m}^{-3}$ . The CDOM content, as given by the coefficient of absorption  $a_{\text{CDOM}}(440 \text{ nm})$ , was also large. Although the mean value of  $a_{\text{CDOM}}(440 \text{ nm})$  was  $2.6 \text{ m}^{-1}$ , in some cases it exceeded  $19 \text{ m}^{-1}$ .

Table 1

Concentration ranges of the main OACs in the lakes under investigation

	$a_{\text{CDOM}}(440\text{nm}), \text{m}^{-1}$	$C_a, \text{mg m}^{-3}$	$C_{\text{SPM}}, \text{g m}^{-3}$	$C_{\text{POM}}, \text{g m}^{-3}$
Mean	2.6	26.9	11.6	9.05
Min	0.3	1.2	0.61	0.58
Max	19.1	336	176	73.9

$a_{\text{CDOM}}(440\text{nm})$  – absorption by chromophoric dissolved organic matter at 440 nm;  $C_a$  – pigment concentration;  $C_{\text{SPM}}$  – suspended particulate matter concentration;  $C_{\text{POM}}$  – suspended particulate organic matter concentration.

The above-mentioned diversity of lake waters was also reflected in the absolute values of the total and specific coefficients of light absorption by phytoplankton. The diversity of the latter is enhanced by the fact that the concentration and composition of phytoplankton pigments, as well as the influence of packaging on these coefficients, depend not only on the trophicity of

waters but also on the depth at which the algae occur. This leads to changes in the absorption properties of phytoplankton with depth; this is illustrated in Figure 1 for one of the lakes. The specific absorption spectra of chlorophyll *a*, normalised to 440 nm, are shown for different depths (fig.1, *a*) and for the surface layer (fig.1, *b*). The depth-dependent shape of the spectrum is additionally modified by the processes of photo- and chromatic adaptation [18]. To keep the description straightforward and to limit the influence of these effects, we have analysed only the data from the surface water layer.

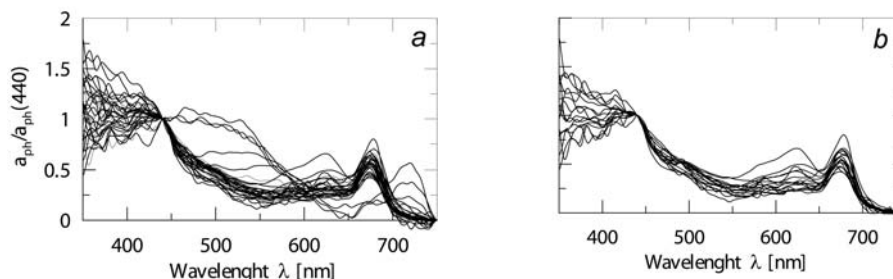


Fig.1. Spectrum of absorption coefficients in Lake Obłęż normalised to 440 nm.  
*a* – data from different depths; *b* – data from the surface layer.

Fig.2 shows the specific absorption coefficient of light by phytoplankton from the surface layer for four wavelengths. With increasing chlorophyll concentration  $C_a$  for all four wavelengths the specific coefficient of absorption  $a_{ph}^*$  decreases. Two factors are thought to be mainly responsible for this differentiation in the absolute values of  $a_{ph}^*$ : the phytoplankton pigment composition and the packaging effect. It is assumed that the variability in  $a_{ph}^*$  for wavelengths around 675 nm chlorophyll absorption peak (fig.1) depends solely on the packaging effect [1, 5]. In sea and ocean waters where chlorophyll concentrations are low, packaging exerts only a minimal influence on  $a_{ph}^*$ , so that its values are close to the total absorption by pigments in the unpackaged state. In other words, the resultant absorption of light by phytoplankton is approximately the sum of absorptions of all its pigments as would be mentioned if they were extracted 'in a solvent'. But with increasing  $C_a$ , packaging has a much greater influence on resultant values of  $a_{ph}^*$ , i.e. the resultant absorptions of phytoplankton in sea and ocean waters in vivo are much smaller than the sum of the coefficients of light absorption by all its pigments. In contrast, the results of our investigations show that the situation in the case of the studied lakes is different. For example, we found that the absorption coefficients  $a_{ph}^*$  for wavelength 675 nm (see fig.2, *d*), that is, for the band where the only absorbent is chlorophyll *a*, is ca  $0.02 \text{ m}^2 \text{ mg}^{-1}$ . Which is a value approximately equal to (and not smaller than) the specific coefficient of the absorption of light of this wavelength by chlorophyll. This implies that in the lakes we investigated the effect of packaging is much less conspicuous – even for large concentrations of chlorophyll – than in sea and ocean waters. Analysis of the subject literature shows that this situation is not specific to the lakes of Polish Pomerania: spectra from Lake Taihu (China) have similar characteristics [18].

A second difference between the  $a_{ph}^*$  spectra measure here and those measured in case I water is due to the fact that all the spectra of light absorption by phytoplankton presented in this paper refer to waters with a considerable concentration of CDOM, their shapes and absolute absorption coefficients  $a_{ph}$  may well be distorted by colloidal and/or particle-bound DOM captured by the glass fiber filter. Binding et al. [19] demonstrated that these substances are retained on GF/F filters and mistakenly incorporated into the phytoplankton absorption signal, which results in an exponential phytoplankton absorption spectrum more typical of CDOM absorption. As can be seen in fig.1, *b*, some of the spectra of light absorption by phytoplankton diverge in shape quite substantially from the usual. This is particularly the case in the short-wave part, where we see an almost monotonic increase in  $a_{ph}^*$  with decreasing wavelength, whereas the short-wave Soret peak is poorly expressed or almost invisible. This may well be

because the methodology applied here is incapable of separating the effects of light absorption by phytoplankton from absorption by colloidal and/or particle-bound DOM. Stæhr and Markager [20], moreover, admit the possibility that the increases in absorption coefficient observed in the region of waves shorter than 440 nm are caused by the high concentration of phaeophytin, the absorption of which peaks around 420 nm.

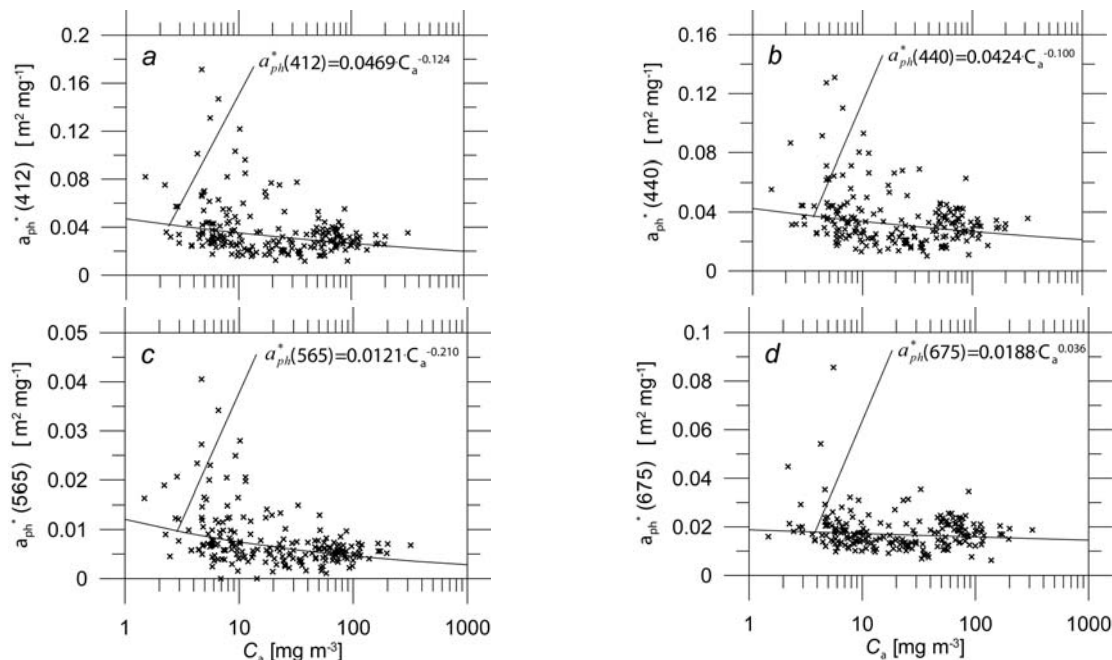


Fig.2. Variations in the chlorophyll *a* absorption coefficients of live phytoplankton  $a_{ph}^*(\lambda)$  ( $\text{m}^2 \text{mg}^{-1}$ ) as a function of the chlorophyll *a* concentration  $C_a$  ( $\text{mg m}^{-3}$ ) at selected wavelengths. *a* – 412, *b* – 440, *c* – 565, *d* – 675 nm.

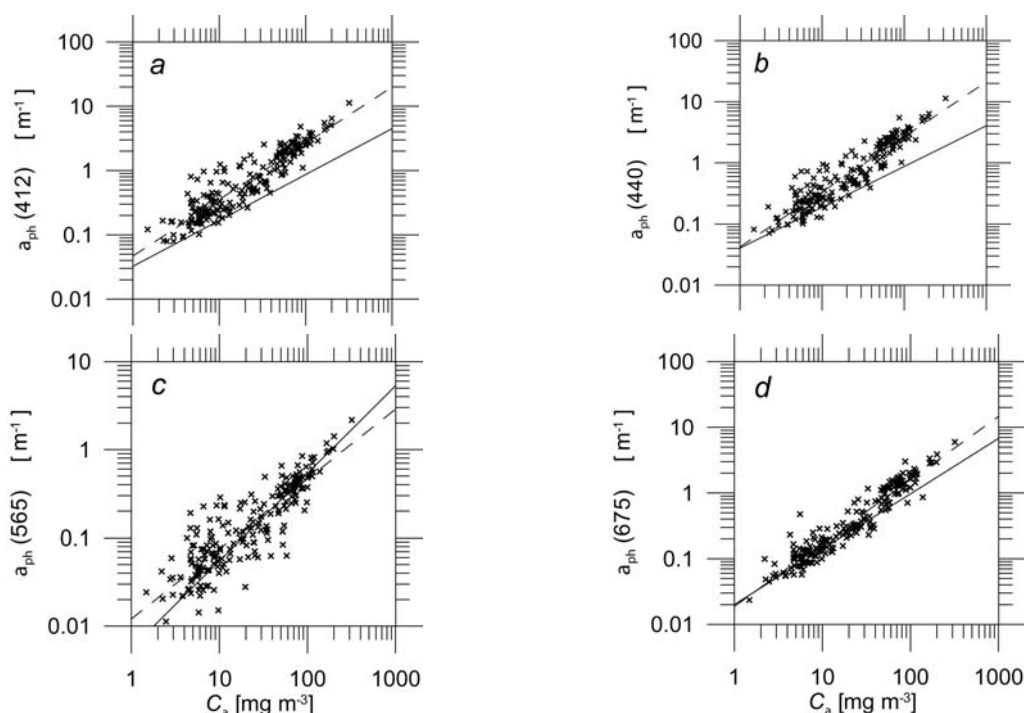


Fig.3. Variations in the phytoplankton absorption coefficients  $a_{ph}(\lambda)$  ( $\text{m}^{-1}$ ) as a function of the chlorophyll *a* concentration  $C_a$  ( $\text{mg m}^{-3}$ ), at selected wavelengths (continuous line – Bricaud's model, dashed line – the new model – described below).

The chlorophyll *a* concentrations  $C_a$  in the samples of lake water examined in this work were usually very high. Our attempts to apply Bricaud's parameterisation to these waters showed that – especially for high  $C_a$  – this parameterisation is unsuitable and should therefore not be used. This is evident from fig.3, which shows the dependence of  $a_{ph}$  on  $C_a$  at four wavelengths. It also shows a similar, modelled relationship worked out using Bricaud's parameterisation (continuous line), and the relationship emerging from our own parameterisation (dashed line), to be discussed shortly. It is clear that with reference to the lakes we studied, the values modelled according to Bricaud's parameterisation for nearly all the wavelengths lie well below the empirically determined values, and the discrepancies are the greater, the higher the chlorophyll *a* concentration.

These discrepancies persuaded us to derive a new parameterisation, resembling the one by Bricaud et al. [1], but based on the absorption coefficients measured in the lakes. To this end we analysed empirical relationships and, using equation (1), approximated the dependence of the coefficient of light absorption on  $C_a$  for the lake waters we investigated. The analyses were carried out for different wavelengths from 400 to 700 nm with a step of 1 nm. The values of the new parameters *A* and *B* with respect to wavelength are given in table 2 and illustrated in fig.4. This figure also shows similar relationships of these parameters, obtained by Bricaud and other authors [1]. In all these models the value of parameter *A* changes with increasing wavelength in the same qualitative way. The reader is reminded at this point that parameter *A* reflects the specific coefficient of absorption for a chlorophyll concentration of  $1 \text{ mg m}^{-3}$ . Since Bricaud's parameterisation was the first to be published and is the best known, we will first describe the differences between that model and our new one. Analysis of parameter *A* in the short-wave region reveals differences in relation to Bricaud's results. Our new model shows two peaks – one at ca 440 nm (as in the Bricaud model) and a second one in the shorter wavelength region at ca 425 nm. Analysis of the subject literature shows that this situation is not specific to the lakes of Polish Pomerania: spectra from lakes in other parts of Europe have similar characteristics (see, for example: [7–9, 21]). The next difference concerns the height of these short-wave peaks. They are noticeably higher than those in Bricaud's parameterisation. Moving towards the longer wavelengths, we see that in lakes the concentrations of accessory pigments absorbing in the 450–520 nm range are lower than those absorbing in the middle regions of the spectrum, i.e. between 520 and 650 nm (probably because of the higher concentrations of the various types of phycobilins). Parameter *B* in our model takes far lower values, which is due to the far smaller variability in absorption coefficients with changes in chlorophyll *a* concentration than in Bricaud's model. This applies in equal measure to the blue and red parts of the spectrum. The middle part of the spectrum is intriguing. Bricaud et al. [1] found parameter *B* in the 570 nm region to be close to zero, which indicates that  $a_{ph}$  varies only slightly with increasing chlorophyll concentration. In the lakes, however, we found a very distinct peak at this wavelength. This is probably due to the presence of phycobilins in the photosynthetic apparatus of lacustrine phytoplankton and to their increasing concentration with rising concentrations of chlorophyll *a*.

Stæhr and Markager [20] and Strömbeck and Pierson [6] modified Bricaud's parameterisation by replacing parameters *A* and *B* determined for oceanic waters with corresponding parameters determined for other natural waters, including those from lakes and estuaries. The values of parameter *A* in Stæhr's and Markager model are the highest across almost the whole range of wavelengths. In contrast, the values of this parameter obtained by Strömbeck and Pierson are the lowest across the same range of wavelengths. The matter is more complicated in the case of parameter *B*. All these authors obtained widely differing values; it is hard to give an unequivocal explanation for the cause of this differentiation.

The question now arises as to the reason for the differences in the values of *A* and *B* as determined by these authors. Strömbeck's and Pierson results were based on a small number of chlorophyll concentrations, varying between 5 to  $40 \text{ mg m}^{-3}$ . Their parameterization may there-

fore not be representative of lakes having chlorophyll concentrations  $< 5 \text{ mg m}^{-3}$  or  $> 40 \text{ mg m}^{-3}$ . Stæhr's and Markager parameterisation presents a somewhat different picture: data not only from estuaries but also from oceans and coastal waters were analysed. With the use of ocean water data, this model begins to resemble that of Bricaud et al. [1]. Again, the differences in the parameterisations by these authors may be due to the selective treatment of  $a_{ph}(\lambda)$  spectra. For example, in Stæhr and Markager [20] we read the following: 'Absorption spectra seriously affected by phaeopigments were identified by high Chl *a* – specific absorption coefficients at around 420 nm compared to 440 nm. These samples and samples collected deeper than 200 m were eliminated from the dataset as they seriously affected model performance'. We decided to only use the spectra from surface samples and, we included waters probably containing quite high amounts of phaeophytin and/or colloidal and/or particle-bound DOM. This was done because some lacustrine spectra may be affected by non phytoplankton absorption. We consider these  $a_{ph}$  spectra to be 'typical' of the lakes we investigated. Our intention was to obtain a model that would provide a comprehensive description of the very great differentiation in light absorption coefficients in the inland waters of this part of Poland.

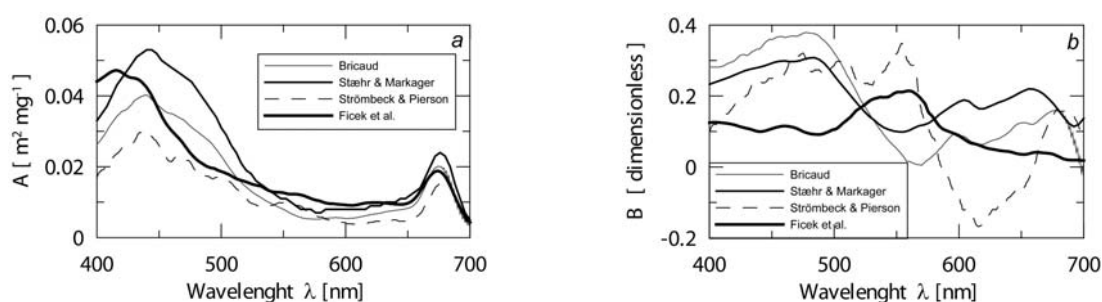


Fig.4. Comparison of the spectral values of  $A$  and  $B$  values obtained by us (see table 2) and from other authors.

Fig.5 illustrates some of the spectra of the absorption coefficient  $a_{ph}^*(\lambda)$  calculated for different values of  $C_a$  from 1 to  $300 \text{ mg m}^{-3}$  obtained from Bricaud's parameterisation and our own one. It shows that the differentiation between the absorption spectra in the blue ( $\sim 440 \text{ nm}$ ) and red light range ( $\sim 665 \text{ nm}$ ) estimated on the basis of our parameterisation is much smaller than that given by Bricaud's model. But the reverse holds where the middle part of the visible light spectrum is concerned (yellow and green light): the differentiation between the spectra estimated with our model is greater than in Bricaud's case. Characteristically, our new parameterisation reveals two distinct peaks (420 and 440 nm) in the short-wave part of the spectrum, whereas Bricaud's model has only one peak ( $\sim 440 \text{ nm}$ ).

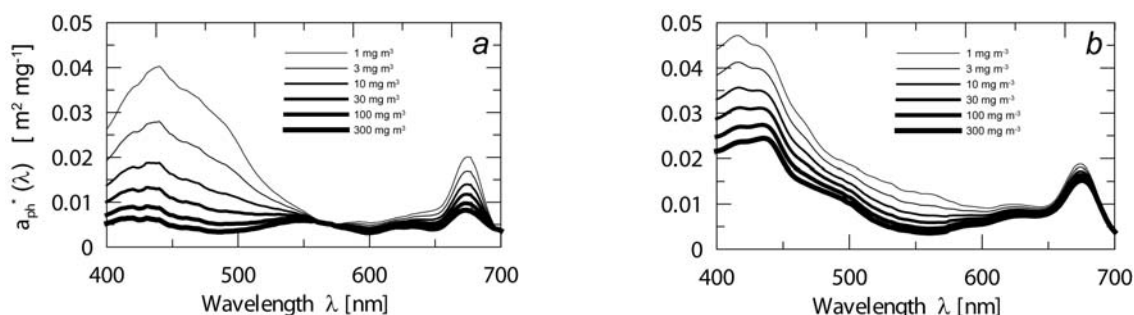


Fig.5. Chlorophyll-specific absorption spectra of live phytoplankton  $a_{ph}^*(\lambda)$  for various chlorophyll  $a$  concentrations  $C_a$  ( $1\text{--}300 \text{ mg m}^{-3}$ ), as reconstructed from (1), with the spectral values of  $A$  and  $B$ .  
a – listed in table 2 in [1]; b – listed in table 2 in this paper.

Table 2

Spectral values of the parameters obtained from fitting the variations of  $a_{ph}^*(\lambda)$  versus the chlorophyll  $a$  concentration  $C_a$  to power laws of the form  $a_{ph}^*(\lambda) = A(\lambda) \cdot C_a^{-B(\lambda)}$

$\lambda$ , nm	$A$	$B$	$\lambda$ , nm	$A$	$B$	$\lambda$ , nm	$A$	$B$	$\lambda$ , nm	$A$	$B$
400	0.0441	0.1250	476	0.0235	0.0988	552	0.0125	0.2114	628	0.0099	0.0494
402	0.0445	0.1259	478	0.0228	0.0964	554	0.0123	0.2110	630	0.0098	0.0482
404	0.0450	0.1261	480	0.0221	0.0943	556	0.0123	0.2121	632	0.0098	0.0468
406	0.0455	0.1258	482	0.0215	0.0929	558	0.0123	0.2139	634	0.0097	0.0457
408	0.0460	0.1252	484	0.0211	0.0922	560	0.0123	0.2146	636	0.0096	0.0449
410	0.0465	0.1245	486	0.0206	0.0916	562	0.0122	0.2132	638	0.0095	0.0443
412	0.0469	0.1238	488	0.0202	0.0917	564	0.0121	0.2097	640	0.0095	0.0436
414	0.0471	0.1229	490	0.0199	0.0925	566	0.0119	0.2046	642	0.0094	0.0421
416	0.0472	0.1218	492	0.0197	0.0946	568	0.0116	0.1983	644	0.0094	0.0400
418	0.0470	0.1205	494	0.0196	0.0977	570	0.0113	0.1907	646	0.0094	0.0380
420	0.0466	0.1187	496	0.0192	0.1000	572	0.0111	0.1821	648	0.0095	0.0365
422	0.0461	0.1167	498	0.0189	0.1039	574	0.0108	0.1676	650	0.0097	0.0356
424	0.0456	0.1144	500	0.0187	0.1055	576	0.0106	0.1518	652	0.0100	0.0353
426	0.0453	0.1123	502	0.0184	0.1084	578	0.0105	0.1452	654	0.0105	0.0358
428	0.0451	0.1106	504	0.0181	0.1139	580	0.0103	0.1361	656	0.0112	0.0374
430	0.0450	0.1091	506	0.0178	0.1204	582	0.0100	0.1258	658	0.0121	0.0394
432	0.0448	0.1074	508	0.0174	0.1265	584	0.0098	0.1165	660	0.0131	0.0409
434	0.0445	0.1052	510	0.0170	0.1319	586	0.0097	0.1098	662	0.0143	0.0414
436	0.0439	0.1029	512	0.0167	0.1379	588	0.0096	0.1056	664	0.0154	0.0410
438	0.0432	0.1009	514	0.0164	0.1443	590	0.0095	0.1026	666	0.0165	0.0404
440	0.0424	0.1000	516	0.0162	0.1529	592	0.0095	0.0999	668	0.0174	0.0398
442	0.0413	0.1001	518	0.0160	0.1602	594	0.0094	0.0971	670	0.0182	0.0393
444	0.0401	0.1013	520	0.0157	0.1647	596	0.0094	0.0944	672	0.0186	0.0385
446	0.0387	0.1032	522	0.0155	0.1693	598	0.0093	0.0913	674	0.0188	0.0373
448	0.0373	0.1056	524	0.0152	0.1742	600	0.0092	0.0876	675	0.0188	0.0364
450	0.0358	0.1080	526	0.0150	0.1797	602	0.0091	0.0834	676	0.0186	0.0353
452	0.0344	0.1102	528	0.0148	0.1854	604	0.0091	0.0787	678	0.0181	0.0325
454	0.0331	0.1121	530	0.0146	0.1897	606	0.0091	0.0739	680	0.0173	0.0291
456	0.0320	0.1138	532	0.0146	0.1922	608	0.0092	0.0699	682	0.0161	0.0256
458	0.0310	0.1150	534	0.0141	0.1941	610	0.0093	0.0672	684	0.0147	0.0226
460	0.0302	0.1154	536	0.0137	0.1961	612	0.0095	0.0656	686	0.0131	0.0208
462	0.0295	0.1150	538	0.0133	0.1968	614	0.0097	0.0639	688	0.0115	0.0198
464	0.0287	0.1141	540	0.0131	0.1964	616	0.0098	0.0616	690	0.0100	0.0195
466	0.0280	0.1128	542	0.0129	0.1966	618	0.0098	0.0588	692	0.0085	0.0193
468	0.0272	0.1111	544	0.0128	0.1983	620	0.0099	0.0560	694	0.0072	0.0193
470	0.0263	0.1085	546	0.0128	0.2028	622	0.0099	0.0536	696	0.0060	0.0192
472	0.0253	0.1052	548	0.0128	0.2074	624	0.0099	0.0519	698	0.0051	0.0186
474	0.0244	0.1018	550	0.0127	0.2104	626	0.0099	0.0505	700	0.0043	0.0185

The final step in this analysis was the empirical validation of this new parameterisation and a comparison of its precision with Bricaud's model as applied to the lakes. Table 3 and fig.6 illustrate the error assessment of the new parameterisation. They also show the errors in the same data obtained using Bricaud's model. As expected, the new parameterisation provided a much better description of the absorption coefficients in Pomeranian lakes. That the systematic errors were reduced to zero is obvious, given that the parameterisation was based on the data analysed here, but the statistical errors were also smaller in comparison with Bricaud's model. With the new model we obtain values corresponding more closely with those measured in Pomeranian lakes. Even so, the scatter of points around the mean is still considerable. This is due to the simplicity of the model and, as already mentioned, to the different trophic indices of the lake waters investigated. Better results would certainly be achieved if the spectra of light absorption by phytoplankton  $a_{ph}$  were parameterised separately for groups of lakes with a similar trophicity, or by constructing multicomponent models that take into account the concentrations of different pigments in phytoplankton (e.g. [21]). If we did that, however, we would for-



feit one of the basic merits of this model, namely, its simplicity and regionality. The work presented here should therefore be treated as preliminary: further work needs to be done.

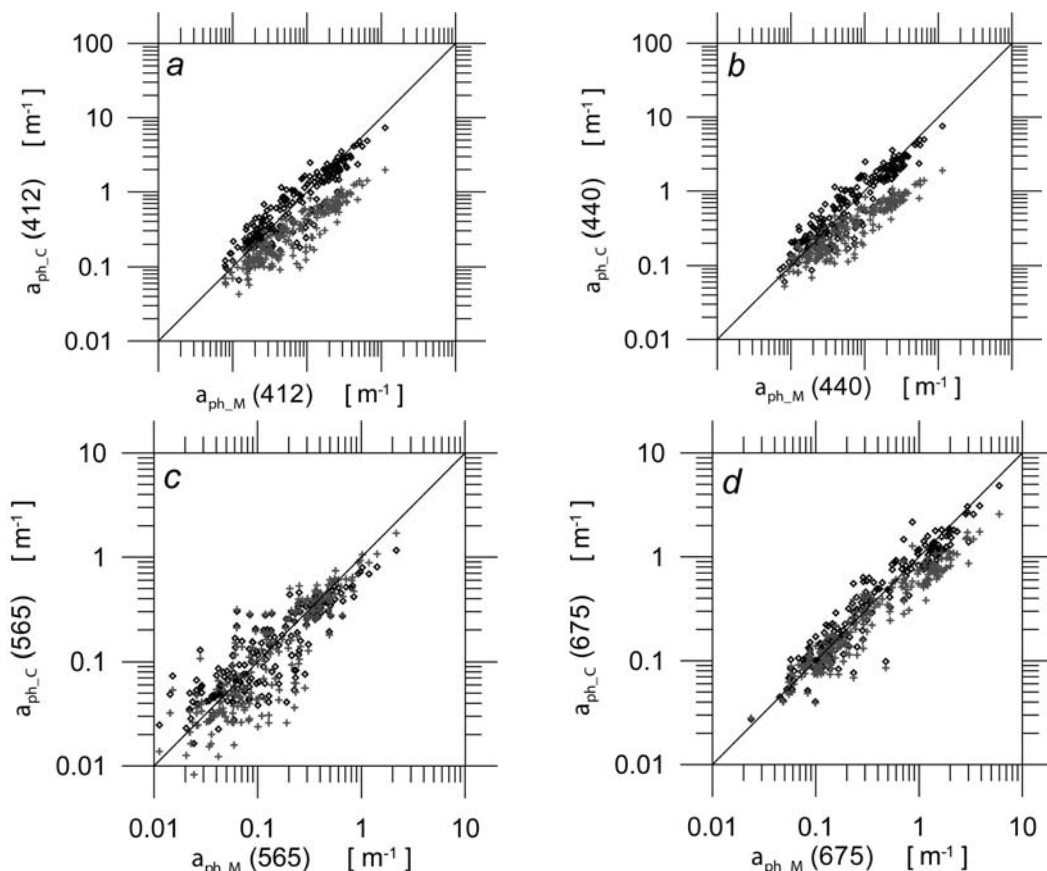


Fig.6. Comparison of the measured spectral absorption coefficients  $a_{ph\ M}$  and the modelled  $a_{ph\ C}$  at selected wavelengths.

$a$  – 412,  $b$  – 440,  $c$  – 565,  $d$  – 675 nm, determined using two models:

( $\diamond$ ) the lake model described in this paper; (+) the model of Bricaud et al. [1].

Table 3

**Relative errors in the phytoplankton absorption coefficient determined using:**  
 **$A$  – the model described in this work;  $B$  – the model of Bricaud et al. [1]**

Wave-length, nm		Arithmetic statistics		Logarithmic statistics			
		systematic error	statistical error	systematic error	standard error factor	statistical error	
		$\langle \varepsilon \rangle$ [%]	$\sigma_\varepsilon$ [%]	$\langle \varepsilon \rangle_g$ [%]	$x$	$\sigma_-$ [%]	$\sigma_+$ [%]
$A$	412	9.55	45.3	0.00	1.56	-36.0	56.2
	440	9.48	47.0	0.00	1.54	-35.2	54.4
	565	8.54	104.0	0.00	1.71	-41.6	71.3
	675	6.01	36.5	0.00	1.42	-29.5	41.9
$B$	412	-52.6	21.9	-57.6	1.62	-38.4	62.4
	440	-46.2	27.1	-52.6	1.67	-40.1	67.0
	565	-5.8	86.3	-15.5	1.80	-44.4	79.8
	675	-20.0	28.8	-25.6	1.46	-31.5	45.9

where  $X_M$  – measured values;  $X_C$  – estimated values (subscript M = measured; subscript C = calculated);

$\varepsilon = (X_C - X_M) / X_M$  – errors;  $\langle \varepsilon \rangle$  – arithmetic mean of errors;  $\sigma_\varepsilon$  – standard deviation of errors (statistical error);  $\langle \varepsilon \rangle_g = 10^{\langle \log(X_C/X_M) \rangle} - 1$  – logarithmic mean of errors;  $\langle \log(X_C/X_M) \rangle$  – mean of  $\log(X_C/X_M)$ ;

$\sigma_{\log}$  – standard deviation of  $\log(X_C/X_M)$ ;  $x = 10^{\sigma_{\log}}$  – standard error factor;  $\sigma_+ = x - 1$  and  $\sigma_- = \frac{1}{x} - 1$ .

This work has shown that Bricaud's parameterisation has only limited applicability to the lakes of Pomerania (Poland). The absorption coefficients calculated using that model, especially for large concentrations of chlorophyll *a*, are underestimated with respect to empirical values. By taking into account the new values of parameters *A* and *B* for lakes, determined in this work, the model gains in precision. The use of these new parameters *A* and *B* in the calculations yields absorption coefficients that are significantly closer to measured values.

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## References

1. Bricaud A., Babin M., Morel A., Claustre H. Variability in the chlorophyll-specific absorption-coefficients of natural phytoplankton – analysis and parameterisation // J. Of Geophys. Res.-Oceans. 1995. V.100. P.13321–13332.
2. Bidigare R.R., Ondrusek M.E., Morrow J.H., Kiefer D.A. In vivo absorption properties of algal pigments // SPIE Ocean Optics, 1990. X 1302. P.290–302.
3. Woźniak B., Dera J., Ficek D., Majchrowski R., Kaczmarek S., Ostrowska M., Koblenz-Mishke O.I. Model of the in vivo spectral absorption of algal pigments. Part 1. Mathematical apparatus // Oceanologia, 2000. V.42 (2). P.177–190.
4. Majchrowski R., Woźniak B., Dera J., Ficek D., Kaczmarek S., Ostrowska M., Koblenz-Mishke O.I. Model of the in vivo spectral absorption of algal pigments. Part 2. Practical applications of the model // Oceanologia, 2000. V.42 (2). P.191–202.
5. Woźniak B., Dera J. Light Absorption in Sea Water // Springer, 2007. 452 p.
6. Reinart A., Paavel B., Pierson D., Strömbeck N. Inherent and apparent optical properties of Lake Peipsi // Estonia, Boreal Environment Research. 2004. V.9. P.429–445.
7. Albert A. Inversion technique for optical remote sensing in shallow water. University of Hamburg, 2004. 187 p.
8. Lee Z., Carder K. Hyperspectral remote sensing, in Remote sensing of coastal aquatic environments // Springer, Dordrecht. P.181–204.
9. Paavel B., Arst H., Herlevi A. Dependence of spectral distribution on inherent optical properties of lake waters on the concentrations of different water constituents // Nordic Hydrology, 2007. V.38(3). P.265–285.
10. Jeffrey S.W., Mantoura R.F.C., Wright S.W. Phytoplankton pigments in oceanography, UNESCO Publishing, 2005. 661 p.
11. Jeffrey S.W., Humphrey G.F. New spectrophotometric equation for determining chlorophyll a, b, c1 and c2, Biochem. Physiol. Pflanz., 1975, 167. P.194–204.
12. Tassan S., Ferrari G.M. An alternative approach to absorption measurements of aquatic particles retained on filters // Limnol. Oceanogr., 1995. V.40 (8). P.1347–1357.
13. Tassan S., Ferrari G.M. A sensitivity analysis of the 'Transmittance-Reflectance' method for measuring light absorption by aquatic particles // J. Plankton Res. 2002. V.24 (8). P.757–774.
14. Butler W.L. Absorption of light by turbid materials // J. Opt. Soc. A m., 1962. V.52(3). P.292–299.
15. Kaczmarek S., Stramski D., Stramska M. The new pathlength amplification factor investigation // Abstract Publ., Baltic Sea Sci. Congr., 2003. Helsinki. P.149.
16. Stramska M., Stramski D., Kaczmarek S., Allison D.B., Schwarz J. Seasonal and regional differentiation of bio-optical properties within the north polar Atlantic // J. Geophys. Res. 2006. 111, C08003. 16 p. doi:10.1029/2005JC003293.
17. Kirk J.T.O. Light and Photosynthesis in Aquatic Ecosystem. Cambridge University Press, 1996. UK. 509 p.
18. Le C., Li Y., Zha D. Sun D. Specific absorption coefficient and the phytoplankton package effect in Lake Taihu. China, Hydrobiologia, 2009. 619. P.27–37.
19. Binding C.E., Jerome J.H., Booty W.G., Bukata R.P. Spectral absorption properties of dissolved and particulate matter in Lake Erie. Remote Sensing of Environment, 2008. 112: P.1702–1711.
20. Staehr P.A., Markager S. Parameterization of the chlorophyll a-specific in vivo light absorption coefficient covering estuarine, coastal and oceanic waters // Intern.J. of Remote Sensing, 2004. V.25(22). P.5117–5130.
21. Ficek D., Kaczmarek S., Stoń-Egiert J., Woźniak B., Majchrowski R., Dera J. Spectra of light absorption by phytoplankton pigments in the Baltic; conclusions to be drawn from a Gaussian analysis of empirical data // Oceanologia. 2004. V.46(4). P.533–555.

