Quantum yield of photosynthesis in the Baltic: a new mathematical expression for remote sensing applications*

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Abstract

Statistical relationships between the quantum yield of photosynthesis Φ and selected environmental factors in the Baltic have been established on the basis of a large quantity of empirical data. The model formula is the product of the theoretical maximum quantum yield $\Phi_{MAX} = 0.125$ atomC quantum^{-1} and five dimensionless factors f_i taking values from 0 do 1: $\Phi = \Phi_{MAX} f_a\, f_\Delta\, f_{c(C_a(0))}\, f_{c(PAR_{inh})}\, f_{E,t}$. To a sufficiently good approximation, each of these factors f_i appears to be

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dependent on one or at most two environmental factors, such as temperature, underwater irradiance, surface concentration of chlorophyll a, absorption properties of phytoplankton and optical depth. These dependences have been determined for Baltic Case 2 waters. The quantum yield Φ, calculated from known values of these environmental factors, is then applicable in the model algorithm for the remote sensing of Baltic primary production. The statistical error of the approximate quantum yields Φ is 62%.

1. Introduction

The quantum yield of phytoplankton photosynthesis Φ[1] in the sea is a key function enabling the rate of primary production of organic matter to be defined on the basis of the quantity of light energy absorbed by the pigments of that phytoplankton. Φ expresses the efficiency of the conversion of CO_2 molecules fixed in the biomass, or of the evolution of O_2 molecules, per quantum of light absorbed (Koblentz-Mishke et al. 1985, Kirk 1994), i.e.,

$$\Phi = \frac{P^B}{PUR^*} = \frac{P^B}{PAR_0\, \tilde{a}^*_{pl}} \approx \frac{P^B}{1.2 PAR\, \tilde{a}^*_{pl}}, \tag{1}$$

where

P^B [molC (mg tot. chl $a)^{-1}$ s^{-1}] – rate of photosynthesis, (also known as the assimilation number), i.e., primary production P in unit time referred to unit mass of chlorophyll a;

PUR^* [Ein (mg tot. chl $a)^{-1}$ s^{-1}] – the number of quanta absorbed by phytoplankton pigments in unit time referred to unit mass of chlorophyll a;

PAR_0 [Ein m^{-2} s^{-1}] and PAR [Ein m^{-2} s^{-1}] – scalar and downward irradiances by sunlight in the PAR spectral range (400–700 nm);

$\tilde{a}^*_{pl}$ [m^2 (mg tot. chl $a)^{-1}$] – mean chlorophyll-specific absorption coefficient for phytoplankton in vivo weighted by the downward irradiance spectrum $E_d(\lambda)$ [Ein m^{-2} s^{-1} nm^{-1}], i.e.,

$$\tilde{a}^*_{pl} = (PAR)^{-1} \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} E_d(\lambda) a^*_{pl}(\lambda) d\lambda \tag{2a}$$

or

$$\tilde{a}^*_{pl} \approx (PAR_0)^{-1} 1.2 \int_{400\,\mathrm{nm}}^{700\,\mathrm{nm}} E_d(\lambda) a^*_{pl}(\lambda) d\lambda, \tag{2b}$$

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

where
a^*_{pl} [m^2 (mg tot. chl $a)^{-1}$] – chlorophyll-specific coefficient of light absorption by phytoplankton in vivo (see Woźniak & Dera (2007)).

The quantum yield Φ as defined above (eq. (1)) depends on the conditions prevailing in the sea and is related to its theoretical maximum value Φ_{MAX}. One of the fundamental photophysiological characteristics of plants, this theoretical limit $\Phi_{MAX} = 0.125$ molC Ein^{-1}, i.e., 0.125 atomC quantum^{-1} of the quantum yield Φ predicted by the Z-scheme of photosynthesis, is one molecule of O_2 evolved per eight quanta absorbed (see, e.g., Govindjee (1975), Falkowski (ed.) (1980), Myers (1980)). But under natural conditions in the sea, which are not ideal for photosynthesis, values of Φ are less than Φ_{MAX}; we analysed this question in our earlier papers (e.g., Woźniak et al. 2002a,b). We showed there that the theoretical yield Φ_{MAX} in the oceans is, to a first approximation, lowered by six physiological, dimensionless factors related to environmental parameters (Woźniak et al. 2002a):

$$\left.\begin{array}{r}\Phi = \Phi_{MAX} f_a\, f_\Delta\, f_{c(N_{inorg})}\, f_{c(\tau)}\, f_{c(PAR_{inh})}\, f_{E,t}\\ \Phi_{MAX} = 0.125\,[\text{atomC quantum}^{-1}] \text{ or } [\text{molC}\,(\text{Ein})^{-1}]\end{array}\right\}. \tag{3}$$

These six dimensionless factors, which can take values from 0 to 1, are:

f_a – a factor accounting for the effect of non-photosynthetic pigment absorption; it describes the decrease in the quantum yield in relation to Φ_{MAX} due to the presence in the plant of photoprotecting pigments that do not transfer absorbed energy to the PS2 reaction centres (RC);

f_Δ – a factor accounting for inefficiency in energy transfer and charge recombination;

$f_{c(N_{inorg})}$ – a factor describing the effect of nutrients on the portion of functional PS2 RC;

$f_{c(\tau)}$ – a factor describing the reduction in the portion of functional PS2 RC at large depths;

$f_{c(PAR_{inh})}$ – a factor describing the reduction in the portion of functional PS2 RC as a result of photoinhibition;

$f_{E,t}$ – a factor describing the classic dependence of photosynthesis on light and temperature (e.g., Morel 1991, Dera 1995, Ficek 2001), also known as the light curve of photosynthetic efficiency at a given temperature.

Our research has shown that each of these factors is a function usually of one or two variables, such as depth in the sea, and the following environmental parameters and optical properties of phytoplankton: underwater irradiance spectra, nutrient concentrations, chlorophyll a

concentration, temperature, spectra of absorption coefficients for all phytoplankton pigments and separately for photosynthetic (antenna) pigments and photoprotecting pigments. The statistical relationships between the six dimensionless factors and these environmental parameters, properties of phytoplankton, and depth in the ocean are given in Woźniak & Dera (2000) and Woźniak et al. (2000).

Empirical verification of this model of quantum yield as applied to oceanic waters produced satisfactory results – the statistical error of the approximate values of the quantum yield Φ is 42%. The model was then successfully applied to the determination and analysis of the distribution of primary production on the basis of known environmental conditions in oceanic Case 1 waters of different trophic index (Woźniak et al. 2003, Ficek et al. 2003). Other authors have also used this model to estimate and analyse primary production in the sea (Mouw & Yoder 2005). In Woźniak et al. (2003) we also showed that this model description of Φ is useful in algorithms for determining primary production in the sea by remote sensing. For this, the three following input parameters of the model, which can be determined from remote sensing data, will suffice: (i) total irradiance in the spectral range of photosynthetically available radiation (400–700 nm) just below the sea surface $PAR(0)$, (ii) sea surface temperature $temp(0)$ and (iii) total concentration of chlorophyll a in the surface water layer $C_a(0)$. In addition, we used certain theoretical and empirical relations between the independent variables in the model expression (3) and the aforementioned parameters ($PAR(0)$, $temp(0)$ and $C_a(0)$).

But our attempts to apply this model of Φ to primary production in the Baltic produced wholly unsatisfactory results. This was the case when primary production was determined on the basis of environmental parameters and the optical properties of phytoplankton at different sea depths in situ, and all the more so, when calculated from parameters estimated from remote sensing data. This must be because Baltic waters are quite different from oceanic waters: they belong to the optically far more complex category of Case 2 waters. The links between the optical, chemical and biological properties of these waters are far more complicated than in the oceans, owing to the considerable, randomly variable inflows into the Baltic of optically active substances from rivers and the seabed. This concerns in particular the factor $f_{c(N_{inorg})}$, a term in the oceanic model for quantum yield, which makes this yield dependent on concentrations of nitrogenous nutrients and other photosynthesis-limiting compounds. Temporally and spatially, the resources of these substances are without doubt more stable in the oceans than in the Baltic.

The objective of the present research was to derive a mathematical model of the quantum yield of photosynthesis applicable in algorithms for the remote sensing of primary production in the Baltic. Because of the complexity and variability of the mix of substances in Baltic waters, this model of the quantum yield's dependence on the environmental parameters in this sea will necessarily be more of a rough approximation than the oceanic model. The model description of the quantum yield of photosynthesis Φ in the Baltic that we now present is the result of the relevant modelling procedure, preceded by a thorough statistical analysis of the extensive bank of empirical data gathered in various regions of the Baltic during cruises of r/v 'Oceania' (IO PAS[2] Sopot) and r/v 'Baltica' (MIR[3] Gdynia) in 1999–2005.

2. The research: description and results

The following mathematical expression for the quantum yield of photosynthesis Φ in the Baltic Sea was derived: it is the product of the theoretical maximum yield $\Phi_{\max}$ (equal to 0.125 molC Ein^{-1}, i.e., 0.125 atomC quantum^{-1}), and five (not six, as for oceanic waters) dimensionless factors:

$$\Phi = \Phi_{MAX} f_a\, f_\Delta\, f_{c(C_a(0))}\, f_{c(PAR_{inh})}\, f_{E,t}. \qquad (4)$$

The dependence of the separate factors f_i on the environmental parameters and their magnitude are given in Table 1, together with their range of variability in the Baltic, estimated from the model. Four out of the five dimensionless factors f_i in eq. (4) have the same meaning as their counterparts in the expression for Φ in oceanic waters (see eq. (3)): the factor accounting for the non-photosynthetic pigment absorption effect (f_a), the factor accounting for inefficiency in energy transfer and charge recombination (f_Δ), the factor describing the reduction in the portion of functional PS2 RC as a result of photoinhibition ($f_{c(PAR_{inh})}$), and the factor related to the classic dependence of photosynthesis on light and temperature ($f_{E,t}$).

However, the effects of the lowering of the quantum yield that result from a smaller number of functional PS2 reaction centres (PS2 RC), in turn due to nutrient deficiency (see factor $f_{c(N_{inorg})}$ in eq. (3)), photoinhibition ($f_{c(PAR_{inh})}$ in eq. (3)) and the disappearance of these centres at large depths ($f_{c(\tau)}$ in eq. (3)), are distributed somewhat differently in the new model expression. The total effect on the value of Φ, which for oceanic waters is described by the product of three factors – $f_c = f_{c(N_{inorg})}\, f_{c(\tau)}\, f_{c(PAR_{inh})}$

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Table 1. Factors f_i determining the quantum yield of photosynthesis in the Baltic Sea expressed by mathematical formulas describing their dependence on abiotic environmental factors at different optical depths τ

No.	Mathematical description of the dependence	Typical range of variability in the Baltic
1	2	3
1	$f_a = \frac{\tilde{a}^*_{pl,\,PSP}}{\tilde{a}^*_{pl}}$, where $\tilde{a}^*_{pl} = f(C_a(0), \tau, PAR(0))$, $\tilde{a}^*_{pl,\,PSP} = f(C_a(0), \tau)$	0.5–1 (about 2 times)
2	$f_\Delta \approx 0.408 \pm 0.105$	nearly constant
3	$f_{c(C_a(0))} = \frac{C_a(0)^{2.48}}{0.15 + C_a(0)^{2.48}}$	0.4–1 (about 2.5 times)
4	$f_{c(PAR_{inh,\,temp})} = \exp\left(\frac{-4860746\,PAR^2}{2.23^{\frac{temp}{10}}}\right)$	0.85–1 (less than 1.2 times)
5	$f_{E,\,t} = \left[1 - \exp\left(\frac{-PUR^*_{PSP}}{5.237\times10^{-7}\,2.03^{\frac{temp}{10}}}\right)\right] \frac{5.237\times10^{-7}\,2.03^{\frac{temp}{10}}}{PUR^*_{PSP}}$	0.05–1 (about 20 times)
6	Φ – as the product, altogether	0.0004–0.051 (about 120 times)
	Φ – as observed values	0.001–0.075 (about 100 times)

where
$C_a(0)$ – surface total chlorophyll a concentration [mg tot. chl a m^{-3}],
PAR – downward irradiance in the PAR spectrum range [Ein m^{-2} s^{-1}],
PUR^*_{PSP} – radiation flux absorbed by photosynthetic pigments [Ein (mg tot. chl a)$^{-1}$ s^{-1}],
$temp$ – ambient water temperature [°C].

Explanations to item 1 – the full mathematical description of the expression for f_a is given by eqs. (4), (9), (10) and in Tables 1, 2, 3 in Woźniak et al. (2007), this volume.

– is described for Baltic waters by the product of two factors: $f_c = f_{c(C_a(0))}\, f_{c(PAR_{inh})}$. The first of these factors, $f_{c(C_a(0))}$, describes the relation between the number of functional PS2 RC and the surface concentration of chlorophyll a, $C_a(0)$, i.e., the trophic index. In principle, it describes the same effects as the factor $f_{c(N_{inorg})}$ in the oceanic model for Φ and is the upshot of the close links between the nutrient concentration in a basin and its trophic index (see, e.g., Woźniak & Dera (2007), chap. 6.1.1). The second factor, standing for the reduction in the portion of PS2 RC in expression (4) for the Baltic, describes, as in the oceanic model (eq. (3)), the reduction in this portion of PS2 RC due to photoinhibition $f_{c(PAR_{inh})}$. In our description of Φ for the Baltic we have omitted the factor $f_{c(\tau)}$. The effects described by this factor seem to be of little significance in the Baltic – we certainly did not notice any in our analyses.

The dependences of the aforementioned five dimensionless factors f_i on environmental parameters, set out in Table 1, were established from empirical research followed by statistical analysis and mathematical modelling in the following three stages.

2.1. Stage I – analysis of factor f_a

To begin with, the effect of the presence of photoprotecting carotenoids (PPC) in the photosynthetic apparatus of phytoplankton on the quantum yield of photosynthesis has to be accounted for. As we know, the energy absorbed by these pigments is not used for photosynthesis. Hence, the true quantum yield of photosynthesis Φ_{tr} is the ratio of the rate of photosynthesis P^B to the number of quanta of PUR^*_{PSP} absorbed solely by the photosynthetic pigments (PSP), i.e., $\Phi_{tr} = P^B/PUR^*_{PSP}$. The quantum yield Φ defined by eq. (1) is therefore smaller than the true value by the factor $f_a = PUR^*_{PSP}/PUR^*$ (where $PUR^* \equiv PUR^*_{pl}$, i.e., the quanta absorbed by all phytoplankton pigments). Since $PUR^*_{PSP} = PAR_0\ \tilde{a}^*_{pl,\,PSP}$ and $PUR^* = PAR_0\ \tilde{a}^*_{pl}$, this factor can be described as the ratio of two mean specific absorption coefficients (by phytoplankton $\tilde{a}^*_{pl}$ and by photosynthetic pigments only $\tilde{a}^*_{pl,\,PSP}$) weighted by the irradiance spectrum (eq. (2)):

$$f_a = \tilde{a}^*_{pl,\,PSP}/\tilde{a}^*_{pl}. \tag{5}$$

In our previous papers (Ficek et al. 2000a, Woźniak et al. 2003) we showed that f_a measured in oceanic waters ranges from c. 0.3 to almost unity and depends largely on the trophic index of the waters in question $C_a(0)$, the level of natural irradiance just below the sea surface, $PAR(0)$ and the optical depth in these waters $\tau \equiv \tau_{PAR}$. Factor f_a usually tends to increase as the values of these three variables do so ($C_a(0)$, $PAR(0)$ and τ or z). Our latest analyses of Baltic Sea data have shown that here, too, the values of f_a depend primarily on these three parameters, but that this dependence is of a somewhat different nature. In particular, the dependence on the chlorophyll concentration $C_a(0)$ is more complex and harder to define precisely. The point is that at the same optical depths in the Baltic and under the same irradiance conditions, f_a measured in different regions of this sea takes different values: these are usually smallest in waters of intermediate trophic index, with concentrations $C_a(0)$ ranging from c. 1.7 to 7.5 mg tot. chl a m^{-3}. On the other hand, they are higher both when $C_a(0)$ is lower in value, i.e., in waters of lower trophic index, and when it is higher, i.e., in waters of higher trophic index. Similarly, the range of variation of f_a in the Baltic, mostly between c. 0.5 and 1, not only differs from that in oceanic waters but is also narrower than in the latter. Moreover, the changes in f_a in the Baltic are subject to a certain seasonality: under otherwise similar conditions, f_a in the 'warm' months (May to September) is usually lower than in the other, 'cool' months. This environmental and seasonal differentiation in f_a in the Baltic is analysed in detail in Woźniak et al. (2007), this volume. There we give an analytical description of f_a in the Baltic, expressed as the ratio $f_a = \tilde{a}^*_{pl,\,PSP}/\tilde{a}^*_{pl}$, in which, for an approximate description of the magnitudes of $\tilde{a}^*_{pl,\,PSP}$ and $\tilde{a}^*_{pl}$, we used the appropriate polynomial functions of three variables: the surface concentration of chlorophyll a, $C_a(0)$, the optical depth in the sea τ, and the irradiance just beneath the sea surface $PAR(0)$. This description has been adopted in the present model of the function Φ for the Baltic (see item 1 in Table 1 and the explanation below this table).

2.2. Stage II – analysis of factors f_Δ, $f_{c(C_a(0))}$ and $f_{c(PAR_{inh})}$

In parallel with the foregoing analysis of factor f_a, the effects of factors f_Δ, $f_{c(C_a(0))}$ and $f_{c(PAR_{inh})}$ on the reduction of Φ with respect to $\Phi_{\max}$ caused by inefficiencies in charge transfer and recombination at the photosynthetic centres (given by f_Δ), and the reduction (for various reasons) in the portion of PS2 RC (given by f_c), were analysed and modelled. In line with our assumptions, the factor f_c is equal to the product $f_c = f_{c(C_a(0))}\, f_{c(PAR_{inh})}$. The combined effect of all these phenomena on the photosynthetic apparatus is also reflected by changes in its fluorescence properties. Moreover, as suggested by, e.g., Kolber & Falkowski (1993), the product of f_Δ and f_c is approximately equal to the maximum change in the quantum yield $\Delta\Phi_{fl}$ of the variable fluorescence of phytoplankton chlorophyll measured in vivo in dark-adapted conditions:

$$\Delta\Phi_{fl} = f_\Delta\, f_c. \tag{6}$$

That is why to define the dependence of factors f_Δ and f_c, along with their components $f_{c(C_a(0))}$ and $f_{c(PAR_{inh})}$, on environmental factors in the Baltic we implemented the results of fluorimetric studies at 60 stations in the Baltic (460 measurement points at different depths) in 1997–2005. The empirical data sets from each measurement point comprised fluorimetrically determined values of the product $f_\Delta\, f_c$ (the methods are described in Ficek et al. (2000b); see also Woźniak et al. (2002a,b)), together with the pigment concentrations, spectral underwater irradiances and corresponding in situ water temperatures. On this basis, with the aid of non-linear regression of multi-variable functions, we were able, after numerous attempts, to write the following relation between the product $f_\Delta\, f_c$ and environmental parameters, which is a good approximation of the empirical data:

$$\Delta\Phi_{fl} \approx f_\Delta \, f_c = \underbrace{c_1}_{f_\Delta} \, \underbrace{\frac{C_a(0)^{c_2}}{c_3 + C_a(0)^{c_2}}}_{f_{c(C_a(0))}} \, \underbrace{\exp\left[\frac{c_4 PAR^2}{(c_5)^{temp/10}}\right]}_{f_{c(PAR_{inh})}}. \tag{7}$$

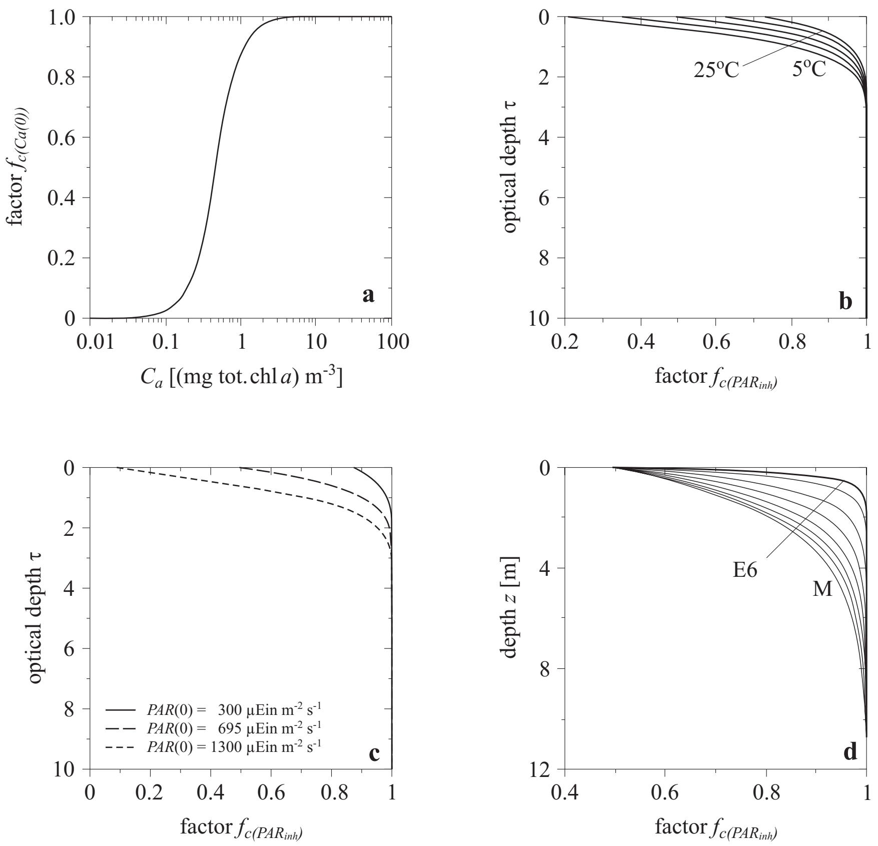

Figure 1. Influence of abiotic environmental factors on the relative number of functional photosynthetic RC in marine phytoplankton, estimated on the basis of model relationships (items 3 and 4 in Table 1): dependence of the factor $f_{c(C_a(0))}$ on the concentration of chlorophyll a in the sea (a); vertical distributions (with respect to the optical depth) of the factor $f_{c(PAR_{inh})}$ determined for a surface irradiance of $PAR(0) = 695$ μEin m^{-2} s^{-1} and five different temperatures: (5, 10, 15, 20, 25 °C) (b); vertical distributions (with respect to the optical depth) of the factor $f_{c(PAR_{inh})}$ determined for temperature $temp = 15$°C and three surface irradiances: $PAR(0) = 300$, 695, 1300 μEin m^{-2} s^{-1} (c); vertical distributions (with respect to the real depth) of the factor $f_{c(PAR_{inh})}$ in different trophic types of sea, determined for surface irradiance $PAR(0) = 695$ μEin m^{-2} s^{-1} and the temperature $temp = 15$°C

The variables and constants in eq. (7) are expressed in the following units: $\Delta\Phi_{fl}$, f_Δ, f_c [dimensionless]; $C_a(0)$ – surface concentration of chlorophyll a [mg tot. chl a m^{-3}]; PAR – the downward irradiance at different depths in the 400–700 nm spectral range [Ein m^{-2} s^{-1}]; $temp$ – ambient water temperature [°C]; the constants take the values: $c_1 = 0.408 \pm 0.105$ [dimensionless]; $c_2 = 2.48$ [dimensionless]; $c_3 = 0.15$ [dimensionless]; $c_4 = -4860746$ [dimensionless]; $c_5 = 2.23$ [dimensionless].

The expression relating f_Δ f_c to the environmental parameters (eq. (7)) is thus the product of three dimensionless factors, which may be interpreted as follows: (i) – the first factor, given by the constant c_1, is f_Δ; (ii) the second factor, $f_{c(C_a(0))}$ describes the effect of trophic index on the number of functional RC in the photosynthetic apparatus (see Figure 1a); (iii) the third factor is $f_{c(PAR_{inh})}$, which describes the decrease, due to light inhibition, in the relative number of functional RC in the surface layer (see Figures 1c and 1d); it, too, is a function of temperature (see Figure 1b).

2.3. Stage III – analysis of factor $f_{E,t}$

The relationship of the quantum yield of photosynthesis to the irradiance is described by the so-called light curves of the yield, which are equivalent to the factor $f_{E,t}$ and are additionally dependent on the seawater temperature. Establishing the dependence of this factor on the irradiance and temperature in the Baltic was the final and most laborious stage of the statistical analyses. We achieved our aim with the aid of the IO PAS bank of the relevant empirical data for the Baltic, which contains historical measurements of primary production and the various environmental parameters governing it, and the sets of measurement data obtained in 2001–2007 (chiefly within the framework of research grant PBZ-KBN 056/2001). More than 3300 measurements of primary production in the Baltic at different depths in the sea at 360 measurement stations were subjected to statistical analysis according to the same scheme as for modelling Φ in oceanic waters (for details, see Ficek (2001), Woźniak et al. (2003)). Here we just give the final form of the expression approximating the dependence of $f_{E,t}$ on the irradiance conditions and the seawater temperature. For this approximation we used the function suggested by Webb et al. (1974):

$$f_{E,t} = \left[1 - \exp\left(-\frac{PUR^*_{PSP}}{KPUR^*_{PSP}(temp)}\right)\right] \frac{KPUR^*_{PSP}(temp)}{PUR^*_{PSP}}, \tag{8}$$

where $KPUR^*_{PSP}(temp)$ depends on the temperature $temp$ [°C] in accordance with the Arrhenius law:

$$KPUR^*_{PSP}(temp) = KPUR^*_{PSP,0}\, Q_{10}^{temp/10}, \tag{9}$$

where $KPUR^*_{PSP,0}$ is the 'photosynthesis saturation PUR_{PSP} energy' at $temp = 0°C$, and Q_{10} is a parameter indicating the multiplication factor of the increase in saturation irradiance due to a temperature rise of $\Delta temp = 10°C$. Using these formulas together, non-linear regression methods applied to two variables yielded the following results for the approximations:

$$KPUR^*_{PSP,0} = 5.237 \times 10^{-7} \quad \text{Ein (mg tot. chl } a)^{-1} \text{ s}^{-1}$$
$$Q_{10} = 2.03. \tag{10}$$

This magnitude was assigned to the model developed in the present work (see item 5 in Table 1). Figure 2 illustrates these light curves, expressed as the dependence of the value of $f_{E,t}$ on the light energy absorbed by the photosynthetic pigments PUR^*_{PSP}.

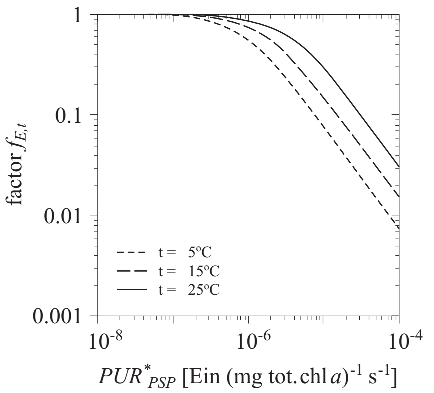

Figure 2. Modelled dependence of the factor $f_{E,t}$ on the energy PUR^*_{PSP} for various temperatures (according to item 5 in Table 1)

3. Verification of the model; main conclusions

Empirical verification was applied to assess the precision of this model description of the quantum yield of photosynthesis in the Baltic. Values of the quantum yield Φ_C, calculated using the model (eq. (4)) and the expressions in Table 1, were compared with values of the quantum yield Φ_M determined empirically (contained in the database), but only for measurement points at which all the parameters enabling the quantum yield to be determined had been measured directly; there were 164 such points. Figure 3 illustrates the results of this verification and Table 2 gives the errors of the model. For comparison, Table 2 also lists the errors of Φ estimated for the Baltic using the earlier oceanic model (Woźniak et al. 2002a,b) (item 2 in Table 2), and also the errors of the quantum yield estimated for oceanic waters (item 1 in Table 2) using the oceanic model (see Table 2 in Woźniak et al. (2002a)).

Figure 3 and Table 2 show that the new model applied to Baltic waters gives far better estimates of Φ (item 3) than the oceanic model applied

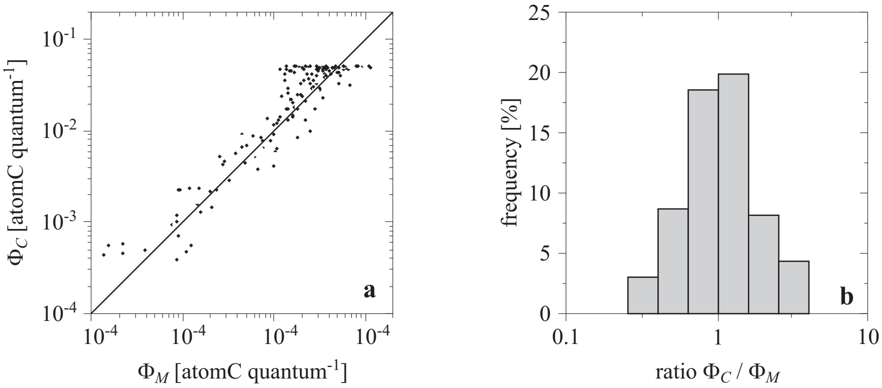

Figure 3. Quantum yield of photosynthesis Φ in the Baltic at different stations and at various depths in the sea: comparison of measured Φ_M and calculated Φ_C according to the model of the yield presented in this paper (eq. (4) and Table 1) (a); histogram of the ratio Φ_C/Φ_M (b)

Table 2. Errors of the estimation of the quantum yield of photosynthesis Φ determined using the model:

1 – oceanic version in the oceans
2 – oceanic version in the Baltic
3 – the new Baltic version 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	6.0	± 42.5	–1.4	1.53	–34.6	53.1
2	24.8	± 120.1	–5.7	2.03	–50.6	102.5
3	6.82	± 62.7	–2.7	1.70	–41.2	70.1

where
$\varepsilon = (\Phi_C - \Phi_M)/\Phi_M$ – relative error,
$< \varepsilon >$ – arithmetic mean of the error,
σ_ε – standard deviation of errors (statistical error),
$< \varepsilon >_{\mathrm{g}} = 10^{[< \log(\Phi_C/\Phi_M) >]} - 1$ – logarithmic mean of errors,
$< \log(\Phi_C/\Phi_M) >$ – mean of $\log(\Phi_C/\Phi_M)$,
$x = 10^{\sigma \log}$ – standard error factor, where $\sigma_{\log}$ – standard deviation of $\log(\Phi_C/\Phi_M)$,
$\sigma_- = \frac{1}{x} - 1$ and $\sigma_+ = x - 1$.

to the Baltic (item 2). Its precision is only slightly less than that of the oceanic model applied to oceanic waters (compare the errors given in items 1 and 3). A further big advantage of this algorithm for the Baltic is that the systematic errors of the estimation are inconsiderable (e.g., $< \varepsilon >_{\mathrm{g}} \approx -2.7\%$); the statistical errors are greater (e.g., $\sigma \approx 63\%$). Likewise, the error factor $x = 1.70$ is relatively small in comparison with the range of variability of the estimated Φ, and is around three orders of magnitude (from c. 0.0001 to c. 0.1 atomC quantum^{-1}).

Another merit of this Baltic model of Φ is that it is dependent solely on environmental parameters measurable by remote sensing (e.g., from satellites). Here, no direct relationship exists between Φ and the nutrient content in the sea, which is difficult to account for in remote sensing algorithms. The main objective of this work – the derivation of a simplified, practicable mathematical description of the quantum yield of photosynthesis in the Baltic – has therefore been achieved.

Besides these rather general conclusions, detailed inferences can be drawn from this research, the most important of which, relating to the nature of the links between Φ and environmental factors, can be formulated as follows:

- The quantum yield of photosynthesis Φ in the Baltic is a complex function of many environmental parameters, such as the level of irradiance, the temperature and trophic index of a basin, as is the case in oceanic waters. Nonetheless, it is readily expressed as the product of $\Phi_{MAX} = 0.125$ atomC quantum^{-1} and five dimensionless factors f_i, less than unity (see eq. (4) and Table 1), each of which depends on one or at most two environmental parameters. Each of these dimensionless factors f_i describes the reduction in measured quantum yields of photosynthesis Φ with respect to its theoretical maximum value Φ_{MAX}. Some of these factors f_i define the reduction in Φ due to the natural (internal) inefficiencies of the photosynthetic apparatus, others account for the reduction in Φ resulting from the less-than-optimum conditions for phytoplankton growth in the Baltic Sea environment.
- The factor f_Δ, which accounts for the natural inefficiency of the photosynthetic apparatus (inefficient energy transfer and charge recombination at the photosynthetic centres), takes a value of nearly 0.41 in the Baltic (Table 1, item 1); it is therefore slightly lower than the value of f_Δ typical of algae in the World Ocean (0.60 – see Woźniak et al. (2002a,b)). That is why measured values of the quantum yield in the Baltic ($\Phi_{MAX}\, f_\Delta$) hardly ever (only in c. 8% of cases) exceed c. 0.051 atomC quantum^{-1}.

- One of the reasons why measured values of Φ are lower than Φ_{MAX} is the presence of photoprotecting pigments in the phytoplankton. In the Baltic, the so-called non-photosynthetic pigment absorption effect factor, f_a, can take a range of values from 0.4 to 1 and depends on the trophic index of the water and depth in the sea. In the Baltic, f_a usually increases with depth, as it does in the oceans, but the dependence of f_a on basin trophic index in the Baltic is more complex than in the oceans. The reader will find a detailed discussion of this question in Woźniak et al. (2007), this volume.

- As in the oceans, a further reason why measured yields are less than Φ_{MAX} is the presence of non-functioning reaction centres (RC) in the photosynthetic apparatus of algae, due, among other things, to photoinhibition or the non-availability of nutrients in waters of low trophic index. The factor describing their combined effect in the Baltic $f_c = f_{c(C_a(0))}\ f_{c(PAR_{inh})}$ takes values from c. 0.2 to 1, as in the oceans, whereby the largest values apply to super-eutrophic basins. In the Baltic, f_c is smallest in the surface water layer and increases monotonically with optical depth to a maximum value of 1 at an optical depth of $\tau > 3$ (see Fig. 1).

- Basin trophic index governs the number of functioning reaction centres RC in cells: their number increases as the concentration of total chlorophyll a does so. The factor describing this influence $f_{c(C_a(0))}$ is related hyperbolically to the surface concentration of chlorophyll $C_a(0)$ in the Baltic (see item 3 in Table 1 and Fig. 1a).

- The irradiance has the greatest influence on the natural differentiation of quantum yields Φ of photosynthesis in the sea. It is well known that when the PAR irradiance is high, Φ is approximately directly proportional to the irradiance. This is the reason why Φ increases with depth throughout the euphotic zone. This effect is described by the light factor $f_{E,t}$, which is additionally dependent on the temperature; its characteristics are much the same in the Baltic and the oceans (see Fig. 2). In the present work, $f_{E,t}$ is described as a function of the energy PUR_{PSP} (i.e., absorbed by the photosynthetic pigments of algae) and the temperature *temp* (see item 5 in Table 1).

- Because the environmental conditions for phytoplankton growth differ in the various Baltic basins, quantum yields of photosynthesis Φ in this sea vary over about three orders of magnitude (item 6 in Table 1); in most cases, however, Φ does not exceed 0.051 atomC quantum^{-1}.

In view of the great complexity of this problem, the results of our statistical analyses and modelling of the quantum yield of photosynthesis cannot be treated as definitive. This research needs to be continued.

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