

Dependence of the photosynthesis quantum yield in oceans on environmental factors*

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Abstract

Statistical relationships between the quantum yield of photosynthesis and selected environmental factors in the ocean have been studied. The underwater irradiance, nutrient content, water temperature and water trophicity (i.e. the surface concentration of chlorophyll $C_a(0)$) have been considered, utilizing a large empirical data base. On the basis of these relationships, a mathematical model of the quantum yield was worked out in which the quantum yield Φ is expressed as a product of the theoretical maximum quantum yield $\Phi_{MAX} = 0.125 \text{ atom C quanta}^{-1}$ and six dimensionless factors. Each of these factors f_i appears to be, to a sufficiently good approximation, dependent on one or two environmental factors and optical depth at most. The model makes it possible to determine the quantum yield from known values of these environmental factors. Empirical verification of the model yielded a positive result – the statistical error of the approximate values of the quantum yield Φ is 42%.

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1. Introduction

The phytoplankton quantum yield of photosynthesis Φ is a measure of the photosynthesis efficiency under the environmental conditions existing at given depths in the sea. It is defined as the ratio of moles of carbon fixed in photosynthesis process per mole of PAR quanta absorbed by phytoplankton pigments, i.e.

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

where

P^B [molC (mg tot. chl a)⁻¹ s⁻¹] – rate of photosynthesis, (also known as the assimilation number), i.e. the production 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}^* [m² (mg tot. chl a)⁻¹] – mean specific absorption coefficient for phytoplankton weighted by the downward irradiance spectrum $E_d(\lambda)$, i.e.

$$\tilde{a}_{pl}^* = (PAR)^{-1} \int_{400 \text{ nm}}^{700 \text{ nm}} E_d(\lambda) a_{pl}^*(\lambda) d\lambda \quad \text{or} \quad (2)$$

$$\tilde{a}_{pl}^* \approx (PAR_0)^{-1} 1.2 \int_{400 \text{ nm}}^{700 \text{ nm}} E_d(\lambda) a_{pl}^*(\lambda) d\lambda.$$

Though the least understood aspect of photosynthesis, the quantum yield as defined here is its most salient characteristic, and must be included in any mathematical model of the process (Bannister 1979, Kiefer & Mitchell 1983, Smith et al. 1989, Platt et al. 1992). That is why it has been the subject of empirical study by numerous authors (see eg. Eppley & Sharp 1975, Steemann Nielsen 1975, Ley & Mauzerall 1982, Koblentz Mishke et al. 1985, Cleveland et al. 1989, Babin et al. 1996) and modelled theoretically and statistically (e.g. Kolber & Falkowski 1992, 1993, Geider et al. 1993, Woźniak et al. 1997a, b). These investigations have shown that the quantum yield of photosynthesis depends on a number of environmental factors, of which the underwater irradiance, the nutrient content, the temperature in the sea, and the trophicity of the waters, i.e. the concentration of chlorophyll $C_a(0)$ at the sea surface have the principle influence on the process. Owing to the vast differences in the values of these parameters in the World Ocean, quantum yields Φ measured in different seas and at

different depths vary over a range of about two orders of magnitude. No one has yet provided a quantitative definition of the relationships between the quantum yield Φ and the environmental parameters that is broad enough to approximate this range of values. Partial solutions to the problem were offered by two simplified mathematical models developed by the teams from Villefranche-sur-Mer (Morel 1991, Morel et al. 1996, Antoine & Morel 1996, Antoine et al. 1996) and Sopot (Woźniak et al. 1992a, b, Woźniak et al. 1995a, b, Dera 1995). However, the accuracy of these models of the quantum yield of photosynthesis is low, because of the numerous simplifications made and the non-recognition of the direct influence of nutrients on the photosynthesis yield.

The aim of this work was to remove these deficiencies from the model. In our new one, we assumed the quantum yield of photosynthesis Φ in the sea to be a complex function of a set of variable environmental factors, such as underwater irradiance, nutrient content, water temperature and water trophicity. For the sake of simplicity, we took only nitrogenous nutrients into account. This step was justified by the results of numerous researchers, who found nitrogen to be the nutrient limiting photosynthesis in most oceanic waters (e.g. Bougis 1976, Koblentz Mishke & Vedernikov 1977, Belayev 1987, Wróblewski 1989, Babin et al. 1996, Morel et al. 1996).

2. Empirical data used in the analysis

The model of the photosynthesis yield was based on the empirical data collected by the authors and those additionally available on the Internet. Two important data bases were made use of at various stages of the modelling:

- The bio-optical data base contained around 2500 sets of empirical data collected at some 600 stations in various regions of the World Ocean (see Table 1 in Majchrowski & Ostrowska 2000). The most important parameters are the primary production $P(z)$, spectral distributions of the downward irradiance $E_d(\lambda, z)$, spectral coefficients of light absorption by phytoplankton $a_{pl}(\lambda, z)$, and chlorophyll a concentration $C_a(z)$. Such magnitudes as the mean daily or instantaneous photosynthesis yield $\Phi(z)$ were determined from these *in situ* data with the aid of eq. (1), as were the corresponding $PAR_0(z)$ irradiances and the energies absorbed by all phytoplankton pigments $PUR^*(z)$, and only by photosynthetic pigments $PUR_{PSP}^*(z)$.
- The fluorimetric database contained over 700 sets of empirical data collected at more than 80 stations in various parts of the World Ocean (see Table 1 in Ficek et al. 2000b). These were the minimal (initial) and maximal *in vivo* induced fluorescences of phytoplankton,

respectively denoted F_0 and F_m according to the Kolber & Falkowski (1993) convention; both were measured in the dark-adapted stage, of phytoplankton where non-photochemical quenching is at a minimum. These fluorescences were measured *in situ* in water samples containing marine algae with the aid of ‘pump-probe’ fluorimeters using the active stimulated method (Kolber & Falkowski 1993, Ostrowska 2001) or the chemical method *in vitro*. In the latter method the fluorescence F_m was measured after the addition of DCMU (see Vedernikov et al. 1990).

Apart from these primary magnitudes, a whole range of physical and chemical parameters of the marine environment, including the nitrogenous nutrient content $N_{\text{inorg}}(z)$, the concentrations of accessory pigments $C_j(z)$ and the temperature $temp(z)$ in the sea, were measured at all the stations.

3. Results of modelling

Although the number of environmental factors is large, only a few have a demonstrable effect on the photosynthesis quantum yield Φ . Our study has made it possible to express the quantum yield Φ as the product of the theoretical maximum quantum yield $\Phi_{MAX} = 0.125 \text{ atom C quanta}^{-1}$ and six dimensionless factors f_i (Woźniak & Dera 2000, 2001). Each less than 1 in value, these factors measure the decrease in Φ compared to Φ_{MAX} due to natural (internal) imperfections in the photosynthetic apparatus or to external conditions unfavourable to plant growth. Such an expression is also compatible with the biophysical models of photosynthesis suggested by other authors (Falkowski & Kiefer 1985, Falkowski et al. 1986, Kolber & Falkowski 1993, Rubin et al. 1994, Rubin 1995, Babin et al. 1996). These six dimensionless factors are: f_a – a non-photosynthetic pigment absorption effect factor which describes the decrease in the observed quantum yield in relation to Φ_{MAX} due to the presence in the plant of photo-protecting pigments that do not transfer absorbed energy to the PS2 reaction centres (RC); f_{Δ} – the inefficiency factor in energy transfer and charge recombination; $f_{c(N_{\text{inorg}})}$ – the factor describing the effect of nutrients on the portion of functional PS2 RC; $f_{c(\tau)}$ – the factor describing the reduction in the portion of functional PS2 RC at large depths; $f_{c(PAR, inh)}$ – the factor describing the reduction in the portion of functional PS2 RC as a result of photoinhibition; $f_{E, t}$ – the classic dependence of photosynthesis on light and temperature (e.g. Morel 1991, Dera 1995, Ficek 2001), also known as the light curve of photosynthesis efficiency at a given temperature.

Each of these factors appears to be, to a good approximation, dependent on one or two environmental factors and optical depth at most. The quantum yield of photosynthesis can therefore be expressed as (Woźniak & Dera 2001):

$$\left. \begin{aligned} \Phi &= \Phi_{\text{MAX}} f_a f_{\Delta} f_{c(N_{\text{inorg}})} f_{c(\tau)} f_{c(\text{PAR}, inh)} f_{E,t} \\ \Phi_{\text{MAX}} &= 0.125 \quad [\text{atom C (quanta)}^{-1}] \text{ or } [\text{mol C (Ein)}^{-1}] \end{aligned} \right\} \quad (3)$$

The magnitude of the separate factors f_i or their dependence on environmental parameters are given in Table 1, together with their range

Table 1. The factors f_i determining the photosynthesis quantum yield (see eq. (3)) expressed through mathematical formulae describing their dependence on abiotic environmental factors, the sea trophicity index $C_a(0)$, and optical depth τ

No.	Mathematical description of the dependence of eq.	Typical magnitude of variability in the World Ocean
1	$f_a = \frac{\tilde{a}_{pl, PSP}^*}{\tilde{a}_{pl}^*}$, where: $a_{pl}^* = f(C_a(0), \tau, PAR(0^+))$ $a_{pl, PSP}^* = f(C_a(0), \tau)$	0.33 ÷ 1 (about 3 times)
2	$f_{\Delta} \approx 0.600 \pm 0.112$	nearly constant
3	$f_{c(\tau)} = 1 - 0.00310 \tau^2$	0.72 ÷ 1 (about 1.4 times)
4	$f_{c(N_{\text{inorg}})} = \frac{N_{\text{inorg}}}{N_{\text{inorg}} + 0.0585}$	0.25 ÷ 1 (about 4 times)
5	$f_{c(\text{PAR}, inh)} = \exp\left(-0.00937 \frac{PAR}{3.049 \times 10^{-5} \times 1.907 \frac{temp}{10}}\right)$	0.85 ÷ 1 (less than 1.2 times)
6	$f_{E,t} = \left[1 - \exp\left(-\frac{PUR_{PSP}^*}{8.545 \times 10^{-7} \times 1.874 \frac{temp}{10}}\right)\right] \times \frac{8.545 \times 10^{-7} \times 1.874 \frac{temp}{10}}{PUR_{PSP}^*}$	0.05 ÷ 1 (about 20 times)
	Φ – as the product, altogether	0.0002 ÷ 0.075 (about 400 times)
	Φ – as observed values	0.001 ÷ 0.075 (about 100 times)

where $C_a(0)$ – surface chlorophyll a concentration [mg tot. chl a m^{-3}]; τ – optical depth in the sea (dimensionless); N_{inorg} – inorganic forms of nitrogen ($N = N(\text{NO}_2) + N(\text{NO}_3) + N(\text{NH}_4)$) [μM]; PAR, inh – scalar irradiance in the PAR spectrum range [$\text{Ein } m^{-2} s^{-1}$]; PUR_{PSP}^* – radiation flux absorbed by photosynthetic pigments [$\text{Ein (mg tot. chl } a)^{-1} s^{-1}$]; $temp$ – ambient water temperature [$^{\circ}\text{C}$].

of variability in the World Ocean, estimated from the model. They were obtained by means of empirical studies, statistical analyses and mathematical modelling, which are described in detail in a number of papers (Ficek et al. 2000a, b, Woźniak & Dera 2000, 2001, Ficek 2001). Here, we shall just give an outline of the most important stages of these investigations.

3.1. Analysis of the factor f_a

The light energy absorbed by the photoprotective carotenoid pigments PPC is not transferred to the photosynthetic centres, and is thus not used in photosynthesis. Hence, the true photosynthesis yield Φ_{tr} is the ratio of the rate of photosynthesis to the number of quanta absorbed solely by the photosynthetic pigments PUR_{PSP}^* [$\text{Ein} (\text{mg tot. chl}a)^{-1} \text{s}^{-1}$], i.e. $\Phi_{tr} = P^B / PUR_{PSP}^*$, and the observed photosynthesis yield Φ , defined by eq. (1), is smaller than the true value by a factor $f_a = PUR_{PSP}^* / PUR^*$. 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 – see eq. (1) in Table 1. The factor f_a can therefore be determined from the model calculations of $\tilde{a}_{pl, PSP}^*$ and \tilde{a}_{pl}^* as the function of the trophicity $C_a(0)$, surface irradiation $PAR(0)$ and optical depth τ (or real z) as input data. The model is described by Woźniak et al. 2000 and Majchrowski et al. 2000. To this end, one can also implement

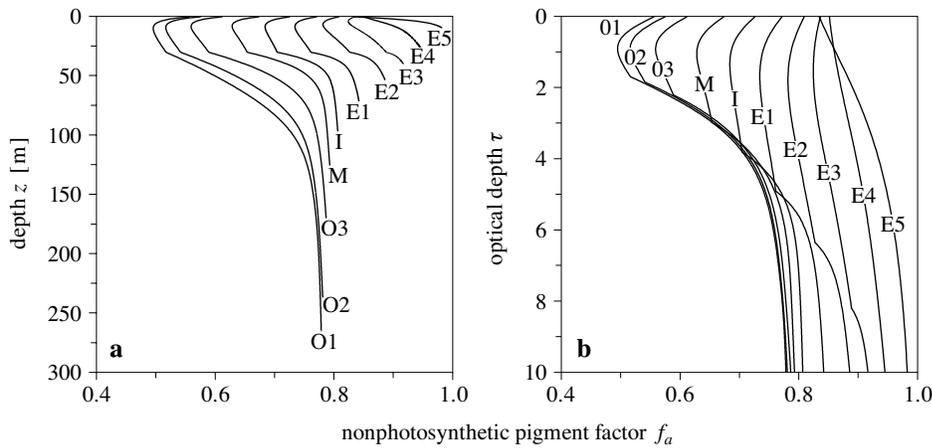


Fig. 1. The modelled vertical distributions of non-photosynthetic pigment factor f_a in different trophic types of sea: dependence on the real depth z [m] (a), dependence on the optical depth τ (b). The symbols of trophic types correspond to the surface chlorophyll a concentrations $C_a(0)$ [$\text{mg tot. chl}a \text{m}^{-3}$]: O1 – 0.035, O2 – 0.07, O3 – 0.15, M – 0.3, I – 0.7, E1 – 1.5, E2 – 3, E3 – 7, E4 – 15, E5 – 30

an approximate model, less time-consuming than the full set of model calculations, which uses the polynomial functions that we derived earlier – $\tilde{a}_{pl, PSP}^* = f(C_a(0), \tau)$ and $\tilde{a}_{pl}^* = f(C_a(0), \tau, PAR(0))$ – given in Appendix after Ficek et al. (2000a). According to the analysis, the factor f_a varies from 0.33 to 1, the value depending on the trophic type of sea and depth in the water column. The values of f_a are usually the highest in eutrophic waters and decrease as waters become progressively more oligotrophic (cf. examples in Fig. 1). It is also characteristic of f_a that it increases with depth.

3.2. Analysis of the factor f_Δ and f_c

Further reasons why actual quantum yields of photosynthesis are smaller than the possible maximum include: (1) the natural inefficiency of the photosynthetic apparatus, due to imperfections in energy transfer and charge recombination, and described by factor f_Δ , and (2) the presence of non-functional PS2 RC. The latter are characterized by factor f_c , the ratio of the number of functional RC to the total number of PS2 RC, i.e. both functional and non-functional. As Kolber & Falkowski (1993) suggested, the product of f_Δ and f_c is approximately equal to the maximum change in the quantum yield of the variable fluorescence of phytoplankton chlorophyll

$$\Delta\Phi_{fl} \approx f_\Delta f_c. \quad (4)$$

In turn, the maximum variable fluorescence yield is given by the ratio of variable and maximum fluorescence of phytoplankton chlorophyll measured *in vivo* in dark-adapted conditions $(F_m - F_0)/F_m$. The empirical material in the fluorimetric data base was analyzed in order to establish the magnitude of the factors f_Δ and f_c .

The fluorescence yields $\Delta\Phi_{fl} \approx f_\Delta f_c$, determined for various stations and depths, differ widely (see Fig. 2a). The vertical profiles $\Delta\Phi_{fl}(z)$, however, display certain characteristic regularities (see Fig. 2b). The tendency for $\Delta\Phi_{fl}$ to rise with increasing trophicity is evident: this increase is due to the larger quantity of nutrients in eutrophic waters.

This nutrient content exerts a positive effect on a portion of the functional PS2 RC. Furthermore, there is for each type of water, a certain optimal depth at which $\Delta\Phi_{fl}$ is the greatest. On moving either up or down from this optimal depth, we find the value of $\Delta\Phi_{fl}$ decreasing, probably because the factor f_c also falls. All these trends were noted earlier (Kolber & Falkowski 1993, Babin et al. 1996). At present, it seems reasonable to explain the decrease in f_c at the surface by photoinhibition, that is, the destructive activity of excess irradiance. On the other hand, the smaller number of functional PS2 RC at greater depths may be due to insufficient irradiance and diminishing numbers of RC. The quantitative description of

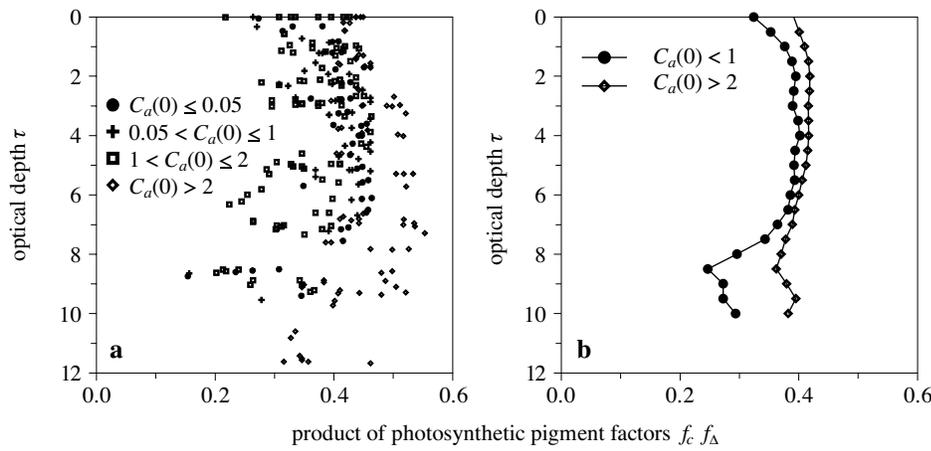


Fig. 2. Vertical profiles (referred to the optical depth τ) of maximum change of variable fluorescence yield of phytoplankton chlorophyll *in vivo* $\Delta\Phi_{fl} \approx f_{\Delta} f_c$ in various trophic types of sea: measured values (a), mean values in two different groups of seas (b)

these trends, i.e. finding the characteristic values of f_{Δ} and presenting f_c as a function of the underwater irradiance in the sea, the optical depth and the nutrient content in the water, was obtained by means of a statistical analysis of the relations between the chlorophyll variable fluorescence $\Delta\Phi_{fl}$ and these parameters of the marine environment.

After numerous attempts to apply non-linear regression methods to a multivariable function, we were able to formulate the following expression describing this function, which gives a good approximation of the empirical data:

$$\Delta\Phi_{fl} \approx f_{\Delta} f_c = c_1 \underbrace{\frac{N_{\text{inorg}}}{N_{\text{inorg}} + c_2}}_{f_c(N_{\text{inorg}})} \underbrace{\exp\left[-c_3 \frac{PAR}{c_4 (c_5)^{temp/10}}\right]}_{f_c(PAR, inh)} \underbrace{(1 - c_6 \tau^2)}_{f_c(\tau)}, \quad (5)$$

where the variables are expressed in the following units: N_{inorg} – the concentration of inorganic nitrogen in [μM]; PAR – the downward irradiance in the interval 400÷700 nm [$\text{Ein m}^{-2} \text{s}^{-1}$]; τ – the optical depth [dimensionless]; *temp* – ambient water temperature [$^{\circ}\text{C}$], and the constants take the values: $c_1 = 0.600 \pm 0.112$ [dimensionless]; $c_2 = 0.0585 \mu\text{M}$; $c_3 = 0.00937$ [dimensionless]; $c_4 = 3.05 \times 10^{-5} \text{Ein m}^{-2} \text{s}^{-1}$; $c_5 = 1.907$ [dimensionless]; $c_6 = 0.0031$ [dimensionless]. As can be seen, the expression for the relation between the product $f_{\Delta} f_c$ and the environmental parameters given by eq. (5) comprises the product of four dimensionless factors. These could be interpreted as follows:

- The first factor, given by the constant c_1 , is the factor f_Δ , postulated by Kolber & Falkowski (1993), describing the ‘inefficiency’ of energy transfer and charge recombination in the photosynthetic apparatus. The value for marine phytoplankton as a whole is typically $f_\Delta = 0.600 \pm 0.112$ (see eq. (2) in Table 1). The value is thus somewhat lower than that ($f_\Delta = 0.65$) given by Kolber & Falkowski (1993). Which of these values is closer to the actual one is hard to state at present.
- The next factor, $f_{c(N_{\text{inorg}})}$, (see eq. (4) in Table 1) describes the effect of nutrient concentrations on the number of functional RC in the photosynthetic apparatus. The expression resembles equations of the Michaelis-Menten type. The constant $c_2 = 0.0585 \mu\text{M}$ is equivalent to the concentration of nitrogenous nutrients, for which the relative number of functional RC falls to half the maximum number. Bearing in mind the natural variability of the nitrogen concentration in the sea, from c. $0.003 \mu\text{M}$ to c. $30 \mu\text{M}$, the factor $f_{c(N_{\text{inorg}})}$ can vary in value by a factor of twenty – from c. 0.05 to c. 1 (see Fig. 3a).
- The third factor in eq. (5) is $f_{c(PAR, inh)}$, which describes the decrease, due to light inhibition, in the relative number of functional RC in the surface layer. This factor correlates well with the absolute level of PAR_0 irradiance in the sea and is also dependent on the water temperature. It is given by relationship (5) in Table 1. The existence of such light inhibition has been demonstrated by other authors (Platt et al. 1980). This inhibition reduces the photosynthesis yield to only a relatively small extent and affects only surface waters. The value of factor $f_{c(PAR, inh)}$ is generally in excess of 0.85 and increases rapidly with depth – see Fig. 3b–d.
- The last factor affecting the relative number of functional RC in the phytoplankton is the optical depth. This is described by the relationship for $f_{c(\tau)}$ given in Table 1 (eq. (3)). Clearly (but see also Figs. 3e and 3f), at large optical depths in the sea there is a distinct drop in the value of $f_{c(\tau)}$, from 1 at the surface to c. 0.73 at depths equal to twice the thickness of the euphotic layer $\tau_{2ze} \approx 9.6$. At present, the mechanism of this phenomenon is not well understood. Presumably, it is brought about by a light deficit and the ‘fading’ of chlorophyll *a* (Wolken 1975, Woźniak & Ostrowska 1990). As a result of such ‘fading’, the photosynthesis RC do not function, even if large concentrations of nutrients and sufficient amounts of photosynthetically useful radiation are present.

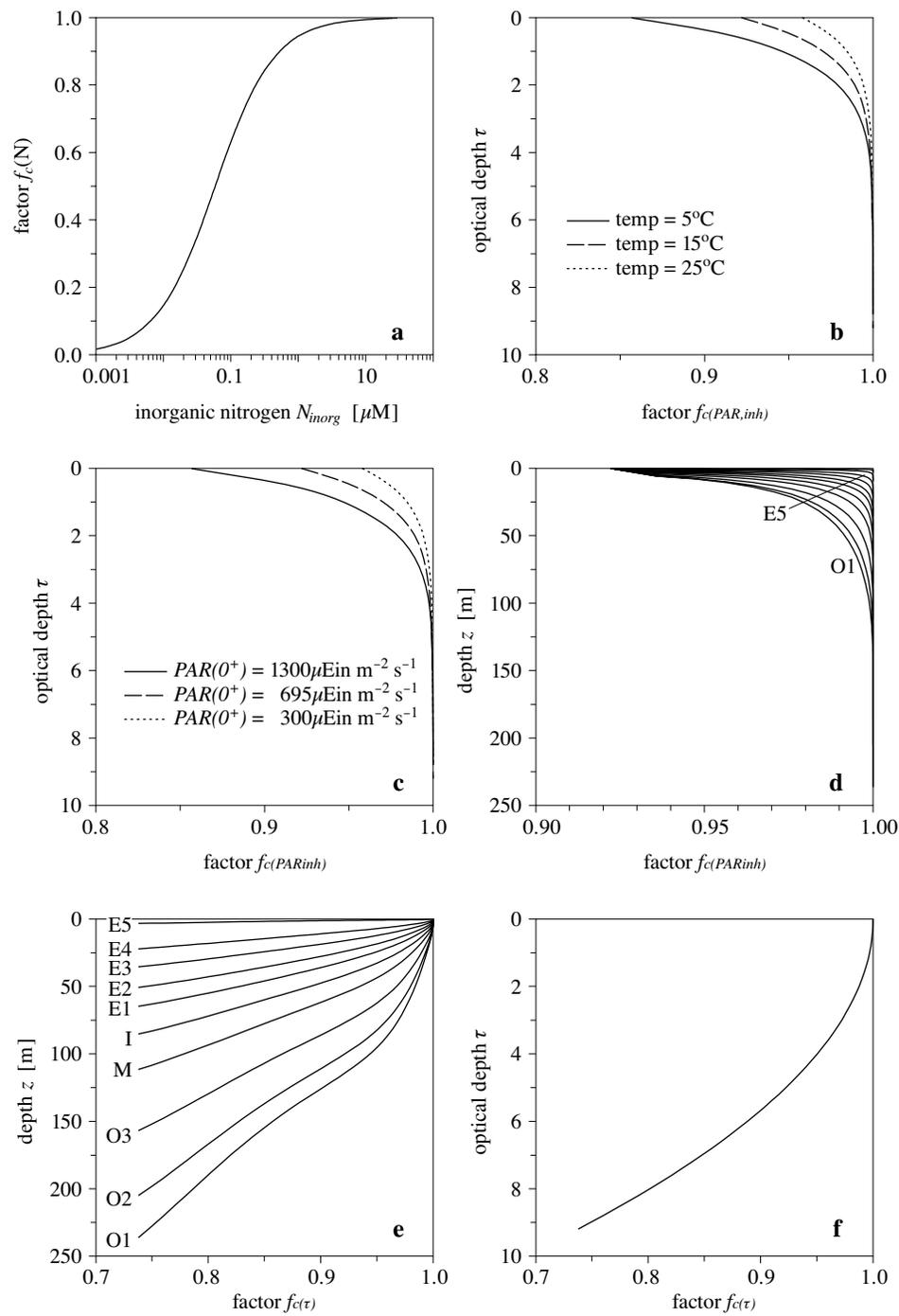


Fig. 3. Influence of abiotic environmental factors on the relative number of functioning photosynthesis RC in marine phytoplankton, estimated on the basis

of model relationships (eqs. (3)–(5) in Table 1): dependence of the factor $f_{c(N)}$ on the concentration of inorganic nitrogen nutrients 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 $PAR(0^+) = 695 \mu\text{Ein m}^{-2} \text{ s}^{-1}$ and three temperatures: ($temp = 5, 15, 25^\circ\text{C}$) (b); vertical distributions (with respect to the optical depth) of the factor $f_{c(PAR, inh)}$ determined for the temperature $temp = 15^\circ\text{C}$ and three surface irradiances: $PAR(0^+) = 300, 695, 1300 \mu\text{Ein m}^{-2} \text{ s}^{-1}$ (c); vertical distributions (with respect to the real depth) of the factor $f_{c(PAR, inh)}$ in different trophic types of sea (see comment in Fig. 1), determined for surface irradiance $PAR(0^+) = 695 \mu\text{Ein m}^{-2} \text{ s}^{-1}$ and the temperature $temp = 15^\circ\text{C}$ (d); vertical distributions (with respect to the real depth) of the factor $f_{c(\tau)}$ in different trophic types of sea (see comment in Fig. 1) (e); vertical distributions (with respect to the optical depth) of the factor $f_{c(\tau)}$ (f)

3.3. Analysis of the factor $f_{E,t}$

The relation between the photosynthesis yield and the irradiance conditions are described by the so-called ‘light curves’ of the yield, which are equivalent to factor $f_{E,t}$ and are additionally dependent on the sea water temperature. Establishing the relationship between $f_{E,t}$ and the irradiance and temperature for the entire phytoplankton in the World Ocean was the final, but also the most labour-intensive stage of our statistical analysis. Some 2500 sets of empirical data from the bio-optical data bank had to be analyzed, including the mean daily quantum yield $\Phi(z)$ at given depths. From these data and the relevant statistical formulas (see above), the mean daily values of $f_{E,t}(z)$ could be determined for particular depths. According to eq. (3), they were

$$f_{E,t}(z) = \frac{\Phi(z)}{0.125 \frac{\text{atom C}}{\text{quanta}} f_a f_\Delta f_{c(N_{\text{inorg}})} f_{c(PAR, inh)} f_{c(\tau)}}, \quad (6)$$

where the factors $f_a, f_\Delta, f_{c(N_{\text{inorg}})}, f_{c(PAR, inh)}, f_{c(\tau)}$ were assumed, or calculated with the aid of the formulas given in Table 1 (eqs. (1)–(5)). The empirical relationship $f_{E,t}(z)$ versus $PAR(z)$ (Fig. 4a) displays considerable scatter, due, among other things, to the influence of the temperature on the yield. This is illustrated, for example, in Fig. 4b, which shows that the plots of the relation $f_{E,t}(z)$ versus $PAR(z)$ are positioned differently for different temperatures. Hence, it is imperative to take account of the effect of temperature on the ‘light curve’ parameters of the photosynthesis yield.

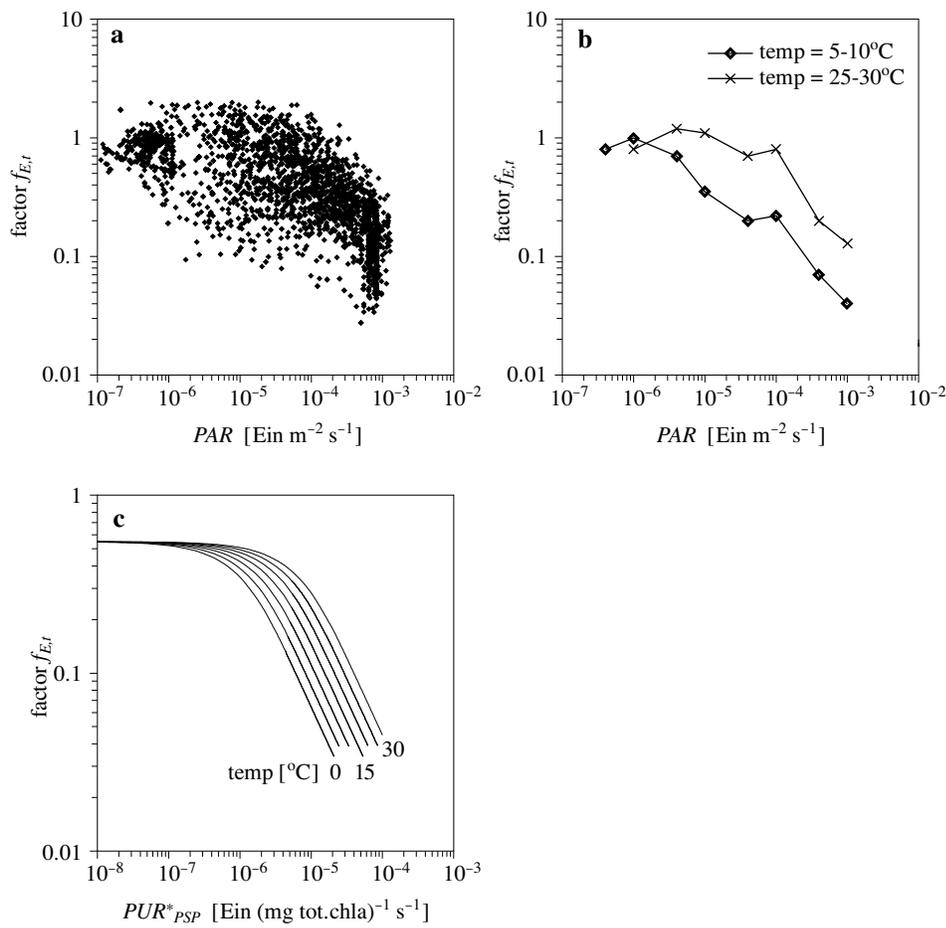


Fig. 4. Observed dependence of mean daily values of the factor $f_{E,t}(z)$ at different depths in the sea on the underwater irradiance PAR or absorbed irradiance PUR^*_{PSP} : for all the points collected in the ‘bio-optical data bank’ (a), averaged for two temperature intervals 5–10°C and 25–30°C (b), modeled dependence of $f_{E,t}$ on the energy PUR^*_{PSP} for various temperatures (according to eq. (6) in Table 1) (c)

The following expression for the light curves of the photosynthetic efficiency at different temperatures was used for performing the approximations on the entire data bank (Webb et al. 1974):

$$f_{E,t} = \left[1 - \exp \left(- \frac{PUR^*_{PSP}}{KPUR^*_{PSP}(temp)} \right) \right] \frac{KPUR^*_{PSP}(temp)}{PUR^*_{PSP}}, \quad (7)$$

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

$$KPUR^*_{PSP}(temp) = KPUR^*_{PSP,0} Q_{10}^{temp/10^\circ C}, \quad (8)$$

where $KPUR_{PSP,0}^*$ is the ‘saturation absorbed irradiance’ at $temp = 0^\circ\text{C}$, and Q_{10} is a parameter indicating the multiplication factor of the increase in saturation irradiance due to a temperature rise of $\Delta temp = 10^\circ\text{C}$.

Using these formulas together, non-linear regression methods applied to two variables (described in detail in Ficek 2001) yielded the following results for the approximations:

$$KPUR_{PSP,0}^* = 8.545 \times 10^{-7} \quad [\text{Ein (mg tot. chl } a)^{-1} \text{ s}^{-1}] \quad (9)$$

$$Q_{10} = 1.874.$$

This magnitude was assigned to the model developed in the present work (see eq. (6) in Table 1). Plots of $f_{E,t}$ versus PUR_{PSP}^* for selected temperatures $temp$ modeled with the aid of this relationship are shown in Fig. 4c.

4. Conclusions and practical comments

As a result of the statistical analysis of the empirical material, a number of regularities have been found linking the photosynthetic quantum yield of marine algae with environmental factors. The most important of them are now given.

- The photosynthesis quantum yield is a complex function of a large number of environmental variables. However the intensity of irradiance, nutrient content, temperature and the water trophicity have a demonstrable effect on the yield. Therefore, this can be expressed as the product of the theoretical maximum quantum yield ($\Phi_{MAX} = 0.125 \text{ atom C quantum}^{-1}$) and six dimensionless factors smaller than unity (see eq. (3)), each of which is, to a good approximation, dependent on one or two environmental parameters and optical depth at most. Each of these dimensionless factors describes a reduction in the photosynthesis quantum yield with respect to the theoretical maximum due to the natural (internal) imperfection of the photosynthetic apparatus, or to less-than-optimal growth conditions.
- The factor f_{Δ} describing the natural imperfection of the photosynthetic apparatus, i.e. the less-than-perfect energy transfer and charge recombination in the photosynthetic RC, takes a value of nearly 0.60 (eq. (2) in Table 1), which is probably characteristic of most algae in the World Ocean. This is why the photosynthesis quantum yields recorded in nature rarely exceed the limiting value ($f_{\Delta} \Phi_{MAX}$) of c. $0.075 \text{ atom C quantum}^{-1}$.

- One of the reasons why observed quantum yields are less than real values is that the set of pigments present in phytoplankton contains photoprotecting pigments. The non-photosynthetic pigment factor f_a describing this effect varies from 0.3 to 1 and depends on the trophic type of sea $C_a(0)$, the surface irradiance $PAR(0^+)$ and the optical depth τ (eq. (1) in Table 1). It usually increases with depth and trophicity (Fig. 1).
- Another reason why observed yields are lower than theoretical maximum ones is that non-functional RC are present in the photosynthetic apparatus of algae. The factor describing this effect, $f_c = f_{c(N_{inorg})} f_{c(\tau)} f_{c(PAR, inh)}$, takes values of from c. 0.2 to 1, the highest being recorded in eutrophic waters (Fig. 2). Moreover, the values of this factor reach a peak in layers where the optical depth τ range is from c. 3 to 6, but decrease in surface and abyssal waters.
- The number of functional RC is determined by the nutrient content of the sea water. This is described by the factor $f_{c(N_{inorg})}$, which is related to the inorganic nitrogen concentration by eq. (4) in Table 1 (see also Fig. 3a).
- The fact that the number of functional RC diminishes in the surface layer is due to photoinhibition, the measure of which is the irradiance- and temperature-dependent factor $f_{c(PAR, inh)}$ (eq. (5) in Table 1 and Figs. 3b, c, d).
- The reduction in the number of functional RC at very great depths is caused by the chlorophyll fading for lack of light. Described by factor $f_{c(\tau)}$, which is related quantitatively with the optical depth (see eq. (3) in Table 1 and Figs. 3e, f), this phenomenon is still rather poorly understood.
- However, it is the light conditions that exert the greatest influence on the natural differentiation in photosynthesis quantum yields in the sea. It is common knowledge that at high irradiance, the quantum yield is practically inversely proportional to the irradiance, which is why the yield increases with depth everywhere in the euphotic zone. This effect is described by the light factor $f_{E,t}$, which is additionally dependent on temperature (see Fig. 4). In this study, $f_{E,t}$ is described in eq. (6) in Table 1 as a function of the irradiance absorbed by the photosynthetic pigments of the algae PUR_{PSP}^* , and the temperature $temp$.
- The quantum yield Φ typically varies under different marine conditions by about 100 times, i.e. two orders of magnitude. This is less than the product of all six dimensionless factors f_i in eq. (3) (with their typical

range of variability), which can reach a figure of 400 (see Table 1). This means that the activities of some of these factors cancel each other out. Light and temperature have the greatest impact on the variability of the natural quantum yield Φ (range about 20 times). Of somewhat less significance is the nutrient content, which may affect the quantum yield by a factor of 4. Finally, threefold variations may occur as a result of variability in the non-photosynthetic pigment factor f_a . The other factors affect the variability in Φ to a much lesser extent.

The model of the photosynthetic yield developed in this paper was now subjected to empirical validation in order to assess its accuracy. Magnitudes of the quantum yield Φ_C calculated using the model (eq. (3) and Table 1) were compared with empirical magnitudes of the yield Φ_M extracted from the bio-optical database. The results of this validation, presented in Fig. 5 and Table 2, show that the errors are relatively small. They are much smaller than those encumbering our earlier model (Woźniak et al. 1992a), which took only the relations between Φ , the trophicity of the water $C_a(0)$ and the underwater irradiance PAR into consideration. For instance, the statistical error in the present model σ is about 42%, whereas in Woźniak's earlier model it was as much as 74%.

Because of the tremendous complexity of the problem, the results of the statistical analysis and modelling of the photosynthesis quantum yield given here should be treated as preliminary. The study needs to be continued and the model developed further.

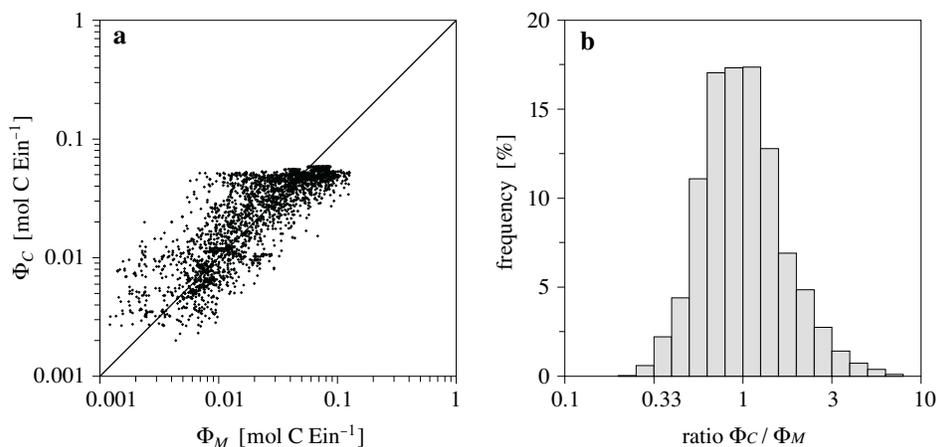


Fig. 5. Comparison of the measured Φ_M and the modelled Φ_C quantum yields (a), and the histogram of the ratio Φ_C/Φ_M (b) at different stations and at various depths in the sea, determined according to the model of yields presented in this paper (eq. (3) and Table 1)

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

Arithmetic statistics		Logarithmic statistics			
systematic	statistical	systematic	standard error factor	statistical	
$\langle \varepsilon \rangle$ [%]	σ_ε [%]	$\langle \varepsilon \rangle_g$ [%]	x	σ_- [%]	σ_+ [%]
6.0	± 42.5	-1.4	1.53	-34.6	53.1

where

$\varepsilon = (\Phi_C - \Phi_M)/\Phi_M$ – errors,

$\langle \varepsilon \rangle$ – arithmetic mean of errors,

σ_ε – standard deviation of errors (statistical error),

$\langle \varepsilon \rangle_g = 10^{[\langle \log(\Phi_C/\Phi_M) \rangle]} - 1$ – logarithmic mean of errors,

$\langle \log(\Phi_C/\Phi_M) \rangle$ – mean of $\log(\Phi_C/\Phi_M)$,

σ_{\log} – standard deviation of $\log(\Phi_C/\Phi_M)$,

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

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

$\sigma_+ = x - 1$.

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Appendix

Polynomial approximation of the non-photosynthetic pigment factor and specific absorption coefficients as a function of water trophicity $C_a(0)$ [mg tot. chl a m^{-3}], surface irradiance $PAR_0(0^+)$ [$\mu\text{Ein m}^{-2} \text{s}^{-1}$] and optical depth τ , according to the equations:

$$f_a = \frac{\tilde{a}_{pl, PSP}^*}{\tilde{a}_{pl}^*}$$

$$\tilde{a}_{pl}^* = \sum_{m=0}^4 \left[\sum_{n=0}^4 A_{mn} (\log(C_a(0)))^n \right] \tau^m + \sum_{m=0}^4 \left[\sum_{n=0}^4 B_{mn} (\log(C_a(0)))^n \right] \tau^m + PAR_0(0^+) \sum_{m=0}^4 \left[\sum_{n=0}^4 C_{mn} (\log(C_a(0)))^n \right] \tau^m$$

$$\tilde{a}_{pl, PSP}^* = \sum_{m=0}^4 \left[\sum_{n=0}^4 A_{mn} (\log(C_a(0)))^n \right] \tau^m.$$

Values of A_{mn}

a. for $0.035 < C_a(0) \leq 1.5$

n \ m	0	1	2	3	4
0	1.382×10^{-2}	-6.329×10^{-3}	-9.281×10^{-3}	-5.333×10^{-3}	-1.195×10^{-3}
1	4.717×10^{-4}	-2.980×10^{-3}	1.460×10^{-2}	1.269×10^{-2}	3.641×10^{-3}
2	-8.151×10^{-5}	7.691×10^{-4}	-5.625×10^{-3}	-6.276×10^{-3}	-2.265×10^{-3}
3	3.254×10^{-5}	-1.270×10^{-4}	6.555×10^{-4}	8.225×10^{-4}	3.218×10^{-4}
4	-2.272×10^{-6}	6.099×10^{-6}	-2.156×10^{-5}	-2.871×10^{-5}	-1.206×10^{-5}

b. for $1.5 < C_a(0) < 70$

n \ m	0	1	2	3	4
0	1.359×10^{-2}	-6.661×10^{-3}	-1.754×10^{-3}	1.293×10^{-3}	-1.661×10^{-4}
1	9.238×10^{-4}	-2.283×10^{-3}	-4.078×10^{-4}	2.144×10^{-3}	-7.524×10^{-4}
2	-2.708×10^{-4}	4.368×10^{-4}	8.568×10^{-4}	-1.295×10^{-3}	4.043×10^{-4}
3	5.401×10^{-5}	-7.769×10^{-5}	-1.056×10^{-4}	1.735×10^{-4}	-5.546×10^{-5}
4	-2.979×10^{-6}	3.940×10^{-6}	5.061×10^{-6}	-8.404×10^{-6}	2.708×10^{-6}

Values of B_{mn}

a. for $0.035 < C_a(0) \leq 1.5$

n \ m	0	1	2	3	4
0	2.536×10^{-3}	-1.639×10^{-3}	-1.651×10^{-3}	-7.143×10^{-4}	-9.046×10^{-5}
1	8.931×10^{-4}	-1.608×10^{-5}	3.912×10^{-3}	3.449×10^{-3}	8.775×10^{-4}
2	-2.102×10^{-4}	3.960×10^{-4}	-1.610×10^{-3}	-1.823×10^{-3}	-6.203×10^{-4}
3	2.463×10^{-5}	-5.496×10^{-5}	1.993×10^{-4}	2.480×10^{-4}	8.994×10^{-5}
4	-1.058×10^{-6}	2.419×10^{-6}	-7.358×10^{-6}	-9.231×10^{-6}	-3.403×10^{-6}

b. for $1.5 < C_a(0) < 70$

$n \backslash m$	0	1	2	3	4
0	2.499×10^{-3}	-1.723×10^{-3}	-1.826×10^{-4}	4.156×10^{-4}	-6.549×10^{-5}
1	9.413×10^{-4}	-1.010×10^{-3}	-5.527×10^{-4}	8.603×10^{-4}	-2.390×10^{-4}
2	-2.556×10^{-4}	3.013×10^{-4}	5.962×10^{-5}	-1.741×10^{-4}	5.277×10^{-5}
3	3.117×10^{-5}	-5.173×10^{-5}	2.531×10^{-5}	-9.859×10^{-7}	-1.458×10^{-6}
4	-1.335×10^{-6}	2.609×10^{-6}	-1.975×10^{-6}	6.795×10^{-7}	-8.609×10^{-8}

Values of C_{mn}

a. for $\tau < \tau_{z=30m}$

$n \backslash m$	0	1	2	3	4
0	-5.484	-7.703×10^{-1}	-3.168×10^{-1}	-5.333×10^{-3}	3.498×10^{-2}
1	$8.595E \times 10^{-2}$	-3.253×10^{-1}	1.815×10^{-1}	4.791×10^{-2}	-4.652×10^{-2}
2	-6.055×10^{-3}	1.522×10^{-1}	-1.618×10^{-1}	-3.010×10^{-3}	2.477×10^{-2}
3	-1.955×10^{-2}	7.841×10^{-3}	2.382×10^{-2}	-1.459×10^{-2}	1.453×10^{-3}
4	3.529×10^{-3}	-7.324×10^{-3}	5.537×10^{-3}	-2.024×10^{-3}	3.284×10^{-4}

b. for $\tau \geq \tau_{z=30m}$

$n \backslash m$	0	1	2	3	4
0	-3.071	8.855	16.99	12.05	2.894
1	-7.338×10^{-1}	-4.255	-8.369	-5.812	-1.319
2	7.143×10^{-2}	8.335×10^{-1}	1.634	1.070	2.167×10^{-1}
3	-1.065×10^{-2}	-7.695×10^{-2}	-1.399×10^{-1}	-8.100×10^{-2}	-1.273×10^{-2}
4	5.096×10^{-4}	2.674×10^{-3}	4.366×10^{-3}	2.066×10^{-3}	1.525×10^{-4}

After Ficek et al. 2000a.