

**Model dependences  
of the deactivation of  
phytoplankton pigment  
excitation energy on  
environmental conditions  
in the sea\***

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**Abstract**

A semi-empirical, physical models have been derived of the quantum yield of the deactivation processes (fluorescence, photosynthesis and heat production) of excited states in phytoplankton pigment molecules. Besides some already known models (photosynthesis and fluorescence), this novel approach incorporates the dependence of the dissipation yield of the excitation energy in phytoplankton pigment molecules on heat. The quantitative dependences of the quantum yields of these three processes on three fundamental parameters of the marine environment are defined: the chlorophyll concentration in the surface water layer  $C_a(0)$  (the basin trophicity), the irradiance  $PAR(z)$  and the temperature  $temp(z)$  at the study site. The model is complemented with two other relevant models describing the quantum yield of photosynthesis and of natural Sun-Induced Chlorophyll *a* Fluorescence (SICF) in the sea, derived earlier by the author or with her

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participation on the basis of statistical analyses of a vast amount of empirical material. The model described in the present paper enables the estimation of the quantum yields of phytoplankton pigment heat production for any region and season, in waters of any trophicity at different depths from the surface to depths of ca 60 m. The model can therefore be used to estimate the yields of these deactivation processes in more than half the thickness of the euphotic zone in oligotrophic waters and in the whole thickness (and deeper) of this zone in mesotrophic and eutrophic waters. In particular these relationships may be useful for a component analysis of the budget of light energy absorbed by phytoplankton pigments, namely, its utilization in fluorescence, photochemical quenching and nonphotochemical radiationless dissipation – i.e. direct heat production.

## 1. Introduction

### 1.1. Presentation of the physical problem

Phytoplankton cells in the sea and other water basins contain numerous sets of pigments, which we generally divide into photosynthetic pigments (PSP) (the main abbreviations and symbols used in the text are listed in the Annex, see page 563) and photoprotecting pigments (PPP) (Goodwin 1952, 1965, Majchrowski 2001). When solar radiation reaches these cells it is spectrally selectively absorbed by the various pigments, which initially leads to the energetic excitation of the molecules. The excitation energy of the molecules of the pigments protecting the cells from excess light (PPP) is usually dissipated radiationlessly in that it is converted into heat that is then conducted to the cell's surroundings. On the other hand, the excitation energy of PSP is conveyed to chlorophyll *a* molecules, which use this energy to produce organic matter by photosynthesis. This energy is only partially consumed during photosynthesis, that is, for the assimilation of carbon. The portion that is not used in this process is radiated in the form of chlorophyll fluorescence in the spectral band ca 685 nm, and/or is also (as in the case of PPP) dissipated radiationlessly (by internal conversion and inter-system crossing), and is ultimately liberated in the form of heat.

Among the above-mentioned ways in which the excitation energy of phytoplankton pigment molecules is dissipated as a result of light absorption, three groups of processes can be distinguished in nature that complement one another in such a way that their summed quantum yields are equal to one. This can be expressed as follows (Kolber & Falkowski 1993):

$$\Phi_{\text{fl}} + \Phi_{\text{ph}} + \Phi_H = 1, \quad (1)$$

where the symbols in equation (1) denote the quantum yields of:

$\Phi_{\text{fl}}$  – fluorescence, that is the ratio of the number of light quanta in the spectra band at 685 nm emitted by chlorophyll *a* to the total number

of quanta from different spectral bands of visible light, absorbed by all phytoplankton pigments (PSP and PPP);

$\Phi_{\text{ph}}$  – the photochemical reactions involved in the photosynthetic assimilation of carbon; in other words, the number of quanta supplying energy to these reactions to – as above – the number of all quanta absorbed;

$\Phi_H$  – direct heat production, i.e. the nonphotochemical radiationless dissipation of the excitation energy of pigments, both PPP and PSP, by way of internal conversion and inter-system crossing. By this yield we here mean the ratio of the number of quanta dissipated as heat (the difference between the number of quanta absorbed by all pigments and the sum of the number of quanta consumed in the assimilation of carbon or emitted in the form of chlorophyll *a* fluorescence) to the number of all absorbed quanta.

## 1.2. The scientific objective of the analyses

The quantum yields of the three excitation dissipation processes ( $\Phi_{\text{fl}}$ ,  $\Phi_{\text{ph}}$ ,  $\Phi_H$ ), taking place under natural conditions in the sea or some other water body and their interrelationships, are diverse and depend on the environmental factors in the water body. Some of the dependences of the quantum yields of these three processes on environmental factors in different seas were studied empirically and mathematically modelled by various authors. Usually they focused on one of the three processes, such as photosynthesis (Koblentz-Mischke 1985, Morel 1991, Antoine et al. 1996, Antoine & Morel 1996, Ficek 2001) or the natural Sun-Induced Chlorophyll *a* Fluorescence (SICF) (e.g. Babin et al. 1995, Maritorea et al. 2000, Morrison 2003, Huot et al. 2005, Huot et al. 2007). What was lacking was a model description of the quantum yield of heat production. On the other hand, the yields of all three groups of processes and the relations between them were investigated experimentally, also using remote sensing methods (Westberry & Siegel 2003). Even so, despite the many empirical studies carried out in different seas and oceans, no coherent statistical or model description has yet been developed for estimating both the absolute values and the relations between all three dissipation processes of phytoplankton pigment excitation energies in the sea.

In view of the above, the present work was undertaken to derive a mathematical model of the dependence of the quantum yield of direct heat production by phytoplankton i.e. non-photochemical radiationless dissipation on the three principal environmental factors governing phytoplankton growth in the sea: the basin trophicity  $C_a(0)$ , the light conditions at different

depths in the water body under scrutiny ( $PAR(z)$ ) and the temperature ( $temp$ ) in the euphotic zone. With such a model it was possible to derive a full model.

Achieving an objective formulated in this way is not a simple matter because the relevant set of empirical data required to establish the empirical constants of such a model and to validate it does not exist. The reason for this is that it is practically impossible to make direct measurements of the heat production. The most one can do is to take simultaneously defined empirical quantum yields of fluorescence  $\Phi_{fl}$  and of photosynthesis  $\Phi_{ph}$  and use them to calculate the yields of the heat production as values complementary to the unity of the sum of the quantum yields of fluorescence and photosynthesis, that is, on the basis of relationships that are rearrangements of equation (1).

Unfortunately, I neither possess nor have been unable to find in the available literature such data containing yield  $\Phi_H$  indirectly determined empirically for different environmental conditions in the sea in quantities sufficient to make statistical generalizations. In this situation, to derive the model of the dependence of the heat production in the sea on environmental factors I have used two models that I developed independently or in cooperation with others, the successively updated versions of which were published in the reports mentioned below. These are models of two complementary means by which the excitation energies of pigment molecules in the photosynthetic apparatus are dissipated, namely, photosynthesis in the sea and the Sun-Induced Chlorophyll *a* Fluorescence (SICF) in the sea. These models and the results of the subsequent modelling performed on their basis will now be described.

## 2. Assumptions and mathematical apparatus of the model

As already mentioned, the model description of the dependence of the heat production in the sea on environmental factors, presented in this work, is a kind of synthesis of two models that I developed earlier independently or with the cooperation of other scientists. The first is the model of photosynthesis in the sea and, in particular, its quantum yield  $\Phi_{ph}$ . It was developed successively, starting in 1992 (Woźniak et al. 1992a,b, 1995, 2002, 2003, 2007, Dera 1995, Ficek 2000), and the latest synthetic version can be found in Ostrowska (2012). This model is founded on the results of statistical analyses of primary production measured in situ, and the basic environmental parameters governing this production (temperature, irradiance, chlorophyll concentration) in different trophic types of basins of the World Ocean, though mainly in the Black and Baltic Seas. The other model I am going to use in this work is the model of the quantum yield

of the natural fluorescence of chlorophyll *a* in the sea  $\Phi_{fl}$ , which I have been working on since 2009 (Ostrowska 2010, 2011); the latest updated version will be found in Ostrowska (2012). It is based on the results of statistical analyses of the yield of this fluorescence  $\Phi_{fl}$ , indirectly determined empirically (on the basis of spectral measurements of the underwater fields of irradiance and radiation) and simultaneous measurements of the fundamental environmental factors governing this fluorescence in various regions of the Atlantic Ocean and Baltic Sea.

These model descriptions enable the above quantum yields  $\Phi_{fl}(z)$  and  $\Phi_{ph}(z)$  to be estimated from the three main environmental parameters governing phytoplankton growth in the sea: basin trophicity, assumed to be the surface concentration of chlorophyll *a*,  $C_a(0)$ ; the light conditions in the sea, the index of which are values of the irradiance  $PAR(z)$  at various depths; and the temperature  $temp(z)$  at different depths. These models are based on empirical material collected in the surface layer of waters, i.e. from the surface down to a depth of ca 60 m. This is equivalent to the water masses in roughly half the euphotic zone in basins with  $C_a(0) < 1 \text{ mg m}^{-3}$ , and almost the whole of the euphotic zone or even transgressing it in other basins. The measurements were carried out in basins of different trophicity and at temperatures ranging from ca 5°C to ca 30°C. We can therefore assume that the relationships are practically universal: to a good approximation they quantitatively describe the processes of photosynthesis and the natural fluorescence of phytoplankton in any ocean or sea basin.

The modelling of the yields of heat processes presented in this work is based on the same principles as the above models of fluorescence and photosynthesis. The appropriately modified assumptions of this modelling are as follows:

- Assumption 1: The model quantum yields of the heat production  $\Phi_H(z)$  at particular depths in the sea are complementary to the unity of the sum of the quantum yields of photosynthesis  $\Phi_{ph}(z)$  and fluorescence  $\Phi_{fl}(z)$ , as emerges from equation (1).
- Assumption 2: The quantum yield of chlorophyll *a* fluorescence as well as the quantum yield of photosynthesis in marine phytoplankton can be described by the product of the theoretically maximum possible values of the yield of these processes and five dimensionless factors taking values from 0 to 1 (Woźniak et al. 2007, Ostrowska 2012):

$$\Phi_{ph} = \Phi_{ph, MAX} f_a f_{\Delta} f_{c(C_a(0))} f_{c(PAR_{inh})} f_{E, t}, \quad (2)$$

$$\Phi_{fl, v} = \Phi_{fl, v, MAX} f_{fl, a} f_{fl, \Delta} f_{fl, c(C_a(0))} f_{fl, c(PAR_{inh})} f_{fl, E, t} =$$

$$= \Phi_{\text{fl},v,\text{MAX}} f_a f_{\Delta} (1 - f_{c(C_a(0))}) f_{c(\text{PAR}_{\text{inh}})} (1 - f_{E,t}), \quad (3)$$

where

$\Phi_{\text{ph},\text{MAX}} = 0.125 \text{ mol atC Ein}^{-1}$  (or  $1 \text{ Ein Ein}^{-1}$ ) is the theoretically maximum possible value of the yield of photosynthesis;

$\Phi_{\text{fl},v,\text{MAX}} = 1 \text{ Ein Ein}^{-1}$  is the theoretically maximum possible value of the yield of fluorescence;

$f_a, f_{\text{fl},a}$  – a factor accounting for the effect of non-photosynthetic pigment absorption; it describes the decrease in the quantum yield in relation to  $\Phi_{\text{MAX}}$  due to the presence in the plant of photoprotecting pigments that do not transfer absorbed energy to the PS2 reaction centres (RC). The excitation energy of PPP is not transferred to a reaction centre, so it cannot be used in photosynthesis or be radiated in the ca 685 nm spectral band by the chlorophyll *a* present in this RC. Hence  $f_{\text{fl},a} = f_a$ ;

$f_{\Delta}, f_{\text{fl},\Delta}$  – the inefficiency factor in energy transfer and charge recombination. This describes the disruption to the functioning of photosynthetic RCs, causing the non-acceptance from pigments of excitation energy that could be further used for photosynthesis, or be radiated in the form of chlorophyll *a* fluorescence in the ca 685 nm band. Therefore  $f_{\text{fl},\Delta} = f_{\Delta}$ ;

$f_{c(C_a(0))}, f_{\text{fl},c(C_a(0))}$  – a factor describing the influence of trophicity (i.e. the surface concentration of chlorophyll *a*,  $C_a(0)$ ) on the number of functioning centres for photosynthesis and fluorescence respectively. Basin trophicity affects the yields of photosynthesis and fluorescence in different ways, factor  $f_{\text{fl},c(C_a(0))}$ , describing the dependence of the number of active PS2 RCs on basin trophicity, is added to  $f_{c(C_a(0))}$  to achieve unity. i.e.  $f_{\text{fl},c(C_a(0))} = 1 - f_{c(C_a(0))}$ ;

$f_{c(\text{PAR}_{\text{inh}})}, f_{\text{fl},c(\text{PAR}_{\text{inh}})}$  – a factor describing the reduction in the portion of functional PS2 RC as a result of photoinhibition. Since these centres are damaged by excess light energy, they do not take up energy that could then be used for the photosynthesis of organic matter or radiated in the form of chlorophyll *a* fluorescence in the ca 685 nm band. Hence  $f_{\text{fl},c(\text{PAR}_{\text{inh}})} = f_{c(\text{PAR}_{\text{inh}})}$ ;

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

relative number of closed RCs, and hence is proportional to the quantum yield of photosynthesis;

$f_{fl,E,t}$  – a factor describing the dependence of fluorescence on light and temperature. The yield of the fluorescence is proportional to the relative number of open RCs, so, factor  $f_{fl,E,t}$ , added to  $f_{E,t}$  gives unity, i.e.  $f_{fl,E,t} = 1 - f_{E,t}$ .

The mathematical dependences of the above factors on the main environmental parameters governing phytoplankton established during empirical studies are given in Table 1 (items 5–9).

- Assumption 3: On the basis of the results of the work of many authors it is assumed that there are two components in the fluorescence of chlorophyll *a*, making up the overall intensity of this fluorescence: the constant component  $F_0$  and the variable component  $F_v$  (see e.g. Kolber & Falkowski 1993, Matorin et al. 1996, Ostrowska et al. 2000, Ostrowska 2001). It is thus assumed that the formula for the quantum yield of fluorescence  $\Phi_{fl}$  can also be expressed as the sum of the two relevant component functions:

$$\Phi_{fl} = \Phi_{fl,0} + \Phi_{fl,v}, \quad (4)$$

where  $\Phi_{fl,0}$  is the quantum yield of the constant component of fluorescence  $F_0$ , while  $\Phi_{fl,v}$  is the quantum yield of the variable component of fluorescence  $F_v$ .

The constant component of fluorescence  $F_0$  is always present, that is, regardless of whether at a given instant the photosynthetic reaction centres RC are open or closed. On the other hand, the variable component  $F_v$  appears only when the RCs are closed and fluorescence is taking place instead of photosynthesis.

- Assumption 4: The quantum yield of the constant component  $\Phi_{fl,0}$  of the natural fluorescence of chlorophyll in a basin in daylight is a function of the surface concentration of chlorophyll *a*,  $C_a(0)$  (and therefore depends on basin trophicity; Ostrowska 2012). The approximate form of this relationship, established as a result of the statistical analyses of numerous sets of empirical data, is given in Table 1 (item 4).

The set of equations, derived from assumptions 1–4, describing the models of the dependences of the quantum yield of heat production in the sea on environmental factors, is given in Table 1.

**Table 1.** Model of the dependence of the quantum yields of the dissipation of excited states in pigment molecules on environmental factors

No.	Basic equations	
1	for fluorescence	$\Phi_{fl} = \Phi_{fl,0} + \Phi_{fl,v} = \Phi_{fl,0} + \Phi_{fl,v,MAX} f_{fl,a} f_{fl,\Delta} \times f_{fl,c(C_a(0))} f_{fl,c(PAR_{inh})} f_{fl,E,t}$
2	for photosynthesis	$\Phi_{ph} = \Phi_{ph,MAX} f_a f_{\Delta} f_{c(C_a(0))} f_{c(PAR_{inh})} f_{E,t}$
3	for other processes dissipating excited states	$\Phi_H = 1 - (\Phi_{fl} + \Phi_{ph})$
No.	Component and factors	
4	$\Phi_{fl,0} = 0.00712C_a(0)^{-0.402}$	see by Ostrowska (2012)
5	$f_a = \frac{\tilde{a}_{pl,PSP}^*}{\tilde{a}_{pl}^*}$ , where $\tilde{a}_{pl,PSP}^* = f(C_a(0), \tau)$	$f_{fl,a} = f_a$ , where definition of $f_a$ and description of $\tilde{a}_{pl}^*$ and $\tilde{a}_{pl,PSP}^*$ see Woźniak et al. (2007), $f_{fl,a}$ see Ostrowska (2012)
6	$f_{\Delta} \approx 0.408 \pm 0.105$	$f_{fl,\Delta} = f_{\Delta}$ , where $f_{\Delta}$ see Woźniak et al. (2007), $f_{fl,\Delta}$ see Ostrowska (2012)
7	$f_{c(PAR_{inh})} = \exp\left(\frac{-4860746PAR^2}{2.23^{temp/10}}\right)$ , where $PAR = PAR(0)e^{-\tau}$	$f_{fl,c(PAR_{inh})} =$ $= f_{c(PAR_{inh})}$ , where $f_{c(PAR_{inh})}$ see Woźniak et al. (2007), $f_{fl,c(PAR_{inh})}$ see Ostrowska (2012)
8	$f_{E,t} = \left[1 - \exp\left(\frac{-PUR_{PSP}^*}{5.23710^{-7} \times 2.03^{temp/10}}\right)\right] \times$ $\times \frac{5.23710^{-7} \times 2.03^{temp/10}}{PUR_{PSP}^*}$ , where $PUR_{PSP}^* = PAR \tilde{a}_{pl,PSP}^*$	$f_{fl,E,t} = 1 - f_{E,t}$ , where $f_{E,t}$ see Woźniak et al. (2007), $f_{fl,E,t}$ see Ostrowska (2012)

**Table 1.** Model of the dependence of the quantum yields of the dissipation of excited states in pigment molecules on environmental factors (*continued*)

No.	Basic equations	
9	$f_{c(C_a(0))} = \frac{C_a(0)^{0.66}}{0.44 + C_a(0)^{0.66}}$	$f_{fl, c(C_a(0))} = 1 - f_{c(C_a(0))},$ where $f_{c(C_a(0))}$ given by Woźniak et al. (1992a,b), $f_{fl, c(C_a(0))}$ see Ostrowska (2012)

where

$C_a(0)$  – total chlorophyll *a* concentration in the surface water layer [ $\text{mg m}^{-3}$ ],

$PAR$  – downward irradiance in the PAR spectral range [ $\mu\text{Ein m}^{-2} \text{s}^{-1}$ ],

$PUR_{\text{PSP}}^*$  – mass-specific radiation flux absorbed by photosynthetic pigments [ $\mu\text{Ein (mg tot.chl } a)^{-1} \text{s}^{-1}$ ],

$temp$  – ambient water temperature [ $^{\circ}\text{C}$ ],

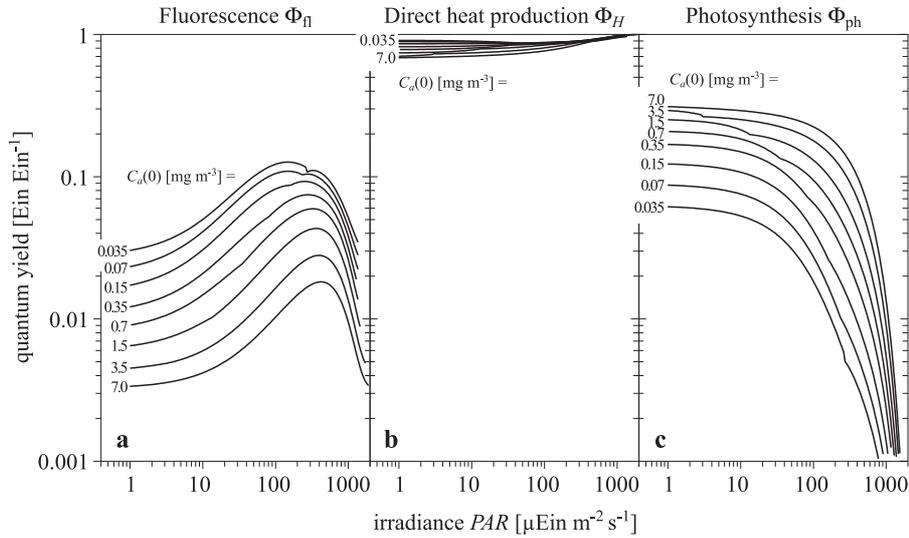
$\tau$  – optical depth in the sea [dimensionless],

$\tilde{a}_{pl}^*$ ,  $\tilde{a}_{pl, \text{PSP}}^*$  [ $\text{m}^2 (\text{mg tot.chl } a)^{-1}$ ] – mean mass-specific coefficient of light absorption of all, and only photosynthetic (PSP) pigments weighted by the irradiance spectrum respectively.

### 3. Modelling results; discussion

The mathematical description of the relationship between the quantum yields of processes of the deactivation of phytoplankton pigment excitation energy and environmental factors, presented in this paper (see eqs. (2)–(4) and Table 1), enables their variability under different conditions in the water column to be tracked down to a depth of ca 60 m. On this basis Figure 1 illustrates the dependences of the quantum yields of all three sets of processes by which excited states in the molecules of all phytoplankton pigments are dissipated on the  $PAR$  irradiance in different trophic types of water. Apart from the dependence of the yield  $\Phi_H$  (Figure 1b), the figure also shows the dependence of the quantum yield of fluorescence  $\Phi_{fl}$  (Figure 1a) and the quantum yield of photosynthesis  $\Phi_{ph}$  (Figure 1c). In order to compare the strongly differentiated ranges of variability of these three yields, their values are presented on a logarithmic scale.

The plots in Figure 1 show that heat production is the most effective of the three possible ways of quenching excited states of PSP molecules in the sea. The quantum yield of heat production far exceeds the other two forms of dissipation in practically all possible configurations of the principal environmental parameters. Values of the quantum yield  $\Phi_H$  usually start from ca 0.65 and in some cases (see the discussion below) can rise to almost 1 (Figure 1b). For the same trophic types of waters



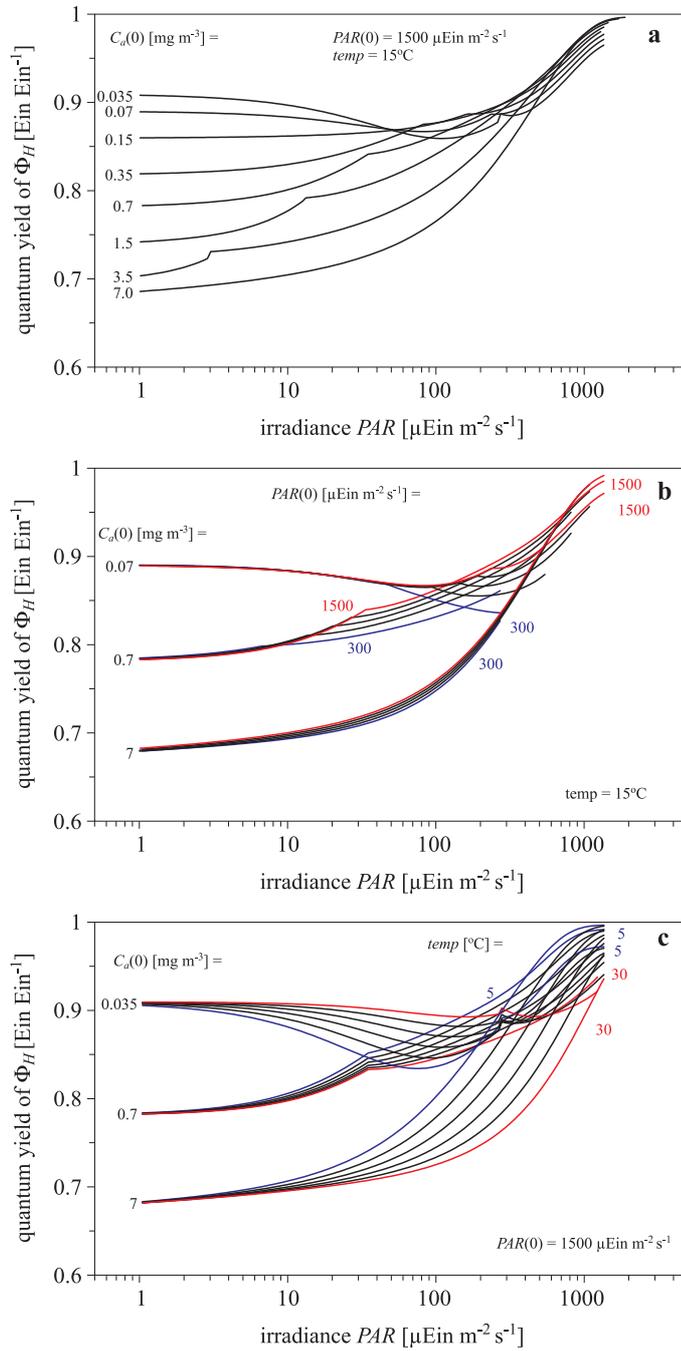
**Figure 1.** Dependence of the model quantum yields of: fluorescence –  $\Phi_{fl}$  (a), direct heat production –  $\Phi_H$  (b), photosynthesis –  $\Phi_{ph}$  (c) on the underwater irradiance  $PAR$  in different trophic types of basins with surface chlorophyll  $a$  concentrations  $C_a(0)$  varying from 0.035 to 7  $\text{mg m}^{-3}$ , for a surface downward irradiance  $PAR = 1500 \mu\text{Ein m}^{-2} \text{s}^{-1}$  and  $temp = 15^\circ\text{C}$ . (Calculated by means of the model formulas given in Table 1)

they are thus from ca 20 to 150 times greater than the quantum yields of fluorescence  $\Phi_{fl}$  (Figure 1a) and usually from 2 to ca 10 times greater than the quantum yields of photosynthesis  $\Phi_{ph}$  (Figure 1c), whereby in the latter case the dependences of quantum yields  $\Phi_H$  and  $\Phi_{ph}$  on basin trophicity  $C_a(0)$  are opposed:  $\Phi_H$  decreases with increasing  $C_a(0)$ , while  $\Phi_{ph}$  rises as  $C_a(0)$  does so. There are two further important features distinguishing the dependences of these three quantum yields on the environmental parameters under scrutiny here. The first one refers to the relative ranges of variability of the three quantum yields under natural conditions in the sea. The yields of fluorescence and photosynthesis vary within quite wide ranges: about one order of magnitude in the case of  $\Phi_{fl}$  and about two orders in the case of  $\Phi_{ph}$ . In contrast, the changes in  $\Phi_H$  are small, even less than twofold. The second feature refers to the directions of their changes as the irradiance conditions change. At low levels of irradiance, over a broad range all three yields remain practically constant, that is, they are independent of the irradiance. At somewhat higher irradiance values (especially starting from ca  $PAR = 10 \mu\text{Ein m}^{-2} \text{s}^{-1}$ )  $\Phi_H$  and  $\Phi_{fl}$  increase as the irradiance does so; but in the case of  $\Phi_{fl}$  this increase is inhibited, and above irradiances in the range ca 100–300  $\mu\text{Ein m}^{-2} \text{s}^{-1}$  values of  $\Phi_{fl}$  fall, whereas  $\Phi_H$  not

only does not fall but continues to rise strongly, almost to the maximum of  $\Phi_H = 1$ . On the other hand,  $\Phi_{ph}$  in medium and high irradiance intervals drops monotonically and ever more strongly with increasing  $PAR$ .

On the other hand the specific nature of the relationship between the quantum yield of heat production  $\Phi_H$  and environmental factors is more precisely illustrated in Figure 2, in which the changes in the values of  $\Phi_H$  are shown on a linear scale. These plots represent the model dependences of this yield on the light conditions in different trophic types of water, where surface chlorophyll  $C_a(0)$  varies from 0.035 to 7 mg m<sup>-3</sup> (a), the surface irradiance  $PAR$  varies from 300 to 1500  $\mu\text{Ein m}^{-2} \text{s}^{-1}$  (b), and  $temp$  varies from 5 to 30°C (c).

As can be seen, the quenching of excited states of phytoplankton pigment molecules is particularly intense under conditions enabling the photoinhibition of the photosynthetic apparatus of algae; it is also triggered by other stress factors. This means that this increase is characteristic of all trophic types of water and at the various possible temperatures in the water under conditions when  $PAR$  reaches its highest possible values (in surface waters), where photoinhibition is particularly intense. This is due, among other things, to the presence of short-wave radiation known as Potentially Destructive Radiation (PDR), i.e. radiation in the spectral interval  $\lambda < 480$  nm, especially that radiation readily absorbed by chlorophyll *a* in the Soret band. This problem is discussed in detail in Woźniak & Dera (2007). Chlorophyll molecules excited in this way have a good chance of shifting from the singlet state to the long-lived triplet state, which enhances the probability of their coming into contact with molecules of oxygen O<sub>2</sub> and being photo-oxidized. To protect itself from such an eventuality, a plant synthesizes photoprotecting carotenoids, whose role it is to capture this excitation energy of chlorophyll molecules and then to dissipate it in a radiationless manner, which increases the quantum yield of heat production  $\Phi_H$ . The principal compound among the photoprotecting carotenoids is zeaxanthin, which is formed from violaxanthin in the so-called xanthophyll cycle (Ruban & Horton 1999). The xanthophyll cycle consists of a whole set of processes, yet to be fully understood, in which mutual conversions of membrane xanthophylls take place in the thylakoids, especially the conversion of violaxanthin to zeaxanthin. The current state of knowledge of this problem is analysed in detail in the papers by Morosinotto et al. (2003), Latowski et al. (2004), Standfuss et al. (2005) and Grzyb et al. (2006).



**Figure 2.** Dependence of the model of quantum yield of direct heat production yield  $\Phi_H$  (calculated on the basis of the model as given in Table 1) on the underwater irradiance  $PAR$  in different trophic types of (*continued on next page*)

**Figure 2.** (*continued*) basins with surface chlorophyll *a* concentrations  $C_a(0)$  varying from 0.035 to 7 mg m<sup>-3</sup>: for a surface irradiance  $PAR = 1500 \mu\text{Ein m}^{-2} \text{s}^{-1}$  and  $temp = 15^\circ\text{C}$  (a); for a surface irradiance  $PAR$  varying from 300 to 1500 (every 300)  $\mu\text{Ein m}^{-2} \text{s}^{-1}$  and  $temp = 15^\circ\text{C}$  (b); for different temperatures in the sea varying from 5 to 30 (every 5)  $^\circ\text{C}$  and a surface irradiance  $PAR = 1500 \mu\text{Ein m}^{-2} \text{s}^{-1}$  (c)

The graphs shown in Figure 2 may also suggest that this quantum yield is dependent not only on natural irradiance but also on other environmental parameters. These are:

- a decrease in yield  $\Phi_H$  with increasing basin trophicity  $C_a(0)$ , visible on all the plots in Figure 2 in the intervals of medium and low  $PAR$  irradiances;
- a distinct variability in the values of yield  $\Phi_H$  dependent on the temperature in the sea, in the intervals of low and medium levels of  $PAR$  irradiances (see Figure 2c). This variability depends on a small drop in the value of  $\Phi_H$  with increasing temperature in eutrophic waters (plot for  $C_a(0) = 7 \text{ mg m}^{-3}$  in Figure 2c) and vice versa, on a continuous monotonic increase in  $\Phi_H$  with rising temperature in oligotrophic basins (plot for  $C_a(0) = 0.035 \text{ mg m}^{-3}$  in Figure 2c).

It should be noted, however, that the variability in the quantum yield of heat production  $\Phi_H$  associated with the basin trophicity  $C_a(0)$  at medium and low irradiances is small. These quantum yields most frequently lie within the limits from  $0.7 \leq \Phi_H \leq 0.9$ , and hence in a narrow range of values with a half-width of roughly 20%. This also applies to the second feature of the variability in  $\Phi_H$ , that is, its model dependence on temperature. We anticipate, therefore, that these features may be encumbered by errors due to the inaccuracy of the model derived and presented in this paper. It was not developed on the basis of a statistical analysis of direct empirical measurements but indirectly, using two other model descriptions – those of the quantum yield of photosynthesis in the sea and the quantum yield of chlorophyll *a* fluorescence. These discrepancies, as already mentioned, may relate especially to the modelled changes in the yield  $\Phi_H$  caused by changes in trophicity and water temperature. Nevertheless, as shown above, the model description of the dependences of  $\Phi_H$  is correct and physically justified.

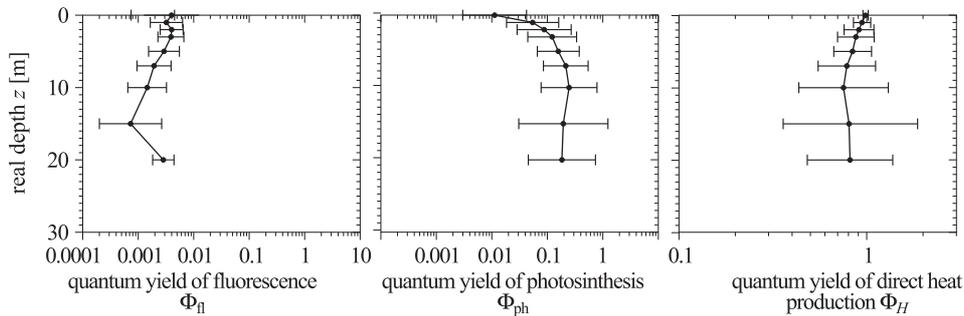
#### 4. Final remarks and conclusion

The aim of this work was to model the quantum yield of heat production (i.e. nonphotochemical radiationless dissipation) by phytoplankton pigments in order to obtain a full description of the dependences of the

deactivation of phytoplankton pigment excitation energy on environmental conditions in the sea. The end result can be regarded as satisfactory, given the current state of knowledge of the functioning of plant communities in the sea. A model was derived (see Table 1) enabling quantum yields to be estimated from values of three basic environmental factors governing the growth of phytoplankton in the sea, i.e. basin trophicity  $C_a(0)$ , and the downward irradiance  $PAR(z)$  and the water temperature  $temp(z)$  at the study site.

The model should be regarded as a preliminary version, for two reasons:

1. In view of the lack of empirical data containing the yields,  $\Phi_H$  were determined in an indirect empirical manner for various environmental conditions in the sea in numbers sufficient for the statistical generalizations to be meaningful. The model was thus developed in the indirect way described in section 2, with the aid of two models of this type that I had derived earlier, either independently or in cooperation with others, namely, the model of natural fluorescence SICF and the model of photosynthesis in the sea. But deriving such a model of the quantum yield of the heat production by phytoplankton pigments from directly determined empirical values of  $\Phi_H$  requires such data to be gathered in amounts sufficient for making the requisite statistical generalizations. Further research in this direction is needed and is being planned.
2. For the same reasons as given above (no empirical material available), this model was not validated to a sufficient degree with empirical data and so the accuracy of the quantum yield  $\Phi_H$  estimated using this model was not assessed. Nonetheless, a number of circumstances indicate that the model is substantially correct, that is, up to 15–20% of the estimated yields. One of them is represented by the vertical profiles of the quantum yields of SICF ( $\Phi_{fl}$ ) (see – Figure 3a), and of photosynthesis ( $\Phi_{ph}$ ) (see – Figure 3b) obtained directly from relevant empirical investigations in the Baltic, and the quantum yield of heat production ( $\Phi_H$ ) (see – Figure 3c), obtained indirectly (as a contribution to unity – see eq. (3)) from empirical values of  $\Phi_{fl}$  and  $\Phi_{ph}$ . The plots in this figure show both the absolute yield  $\Phi_H$  and the nature of its variability with irradiance, which decreases with increasing depth; they correspond to the modelled regularities (see Figures 1 and 2) governing the changes in the quantum yield  $\Phi_H$  caused by changes in  $PAR$  irradiance in the sea. Likewise, the nature of the spatial variations in  $\Phi_H$  over many seasons in 1992–1997, investigated in the north-western Sargasso Sea and presented in the form of graphs in Westberry & Siegel (2003) resembles to



**Figure 3.** Vertical profiles of the averaged quantum yields (and their standard deviations) of three processes taking place in phytoplankton cells: a) the natural fluorescence of chlorophyll *a*, b) photosynthesis, and c) direct heat production. These relationships were worked out for 13 measurement stations in different regions of the Baltic in 1999–2003 (after Woźniak & Tyszka 2006 – unpublished report)

a significant extent the modelled regularities described in the present paper. Regardless of these favourable circumstances, however, the model will have to be properly validated, a subject which I will now be focusing on.

Described set of these three models used simultaneously can be used to balance the quantum yields of the deactivation of the excited states of molecules of all pigments or just chlorophyll *a* in the sea. This will be applied in the next work, the aim of which will be to characterize quantitatively the quantum yields of the chlorophyll *a* fluorescence and its quenchings in different marine system of the World Ocean (see Ostrowska et al. (2012) – in this volume).

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**Annex****List of the abbreviations and symbols used in the text**

Symbol	Denotes	Units
1	2	3
$a$	Coefficient of light absorption	$\text{m}^{-1}$
$a_{\text{pl}}$	Coefficient of light absorption by phytoplankton	$\text{m}^{-1}$
$\tilde{a}_{\text{pl}}$	Mean absorption coefficient for all phytoplankton pigments weighted by the irradiance spectrum	$\text{m}^{-1}$
$\tilde{a}_{\text{pl}}^*$	Mean mass-specific absorption coefficient for all pigments weighted by the irradiance spectrum	$\text{m}^2(\text{mg tot. chl } a)^{-1}$
$\tilde{a}_{\text{pl, PSP}}^*$	Mean mass-specific absorption coefficient of photosynthetic pigments weighted by the irradiance spectrum	$\text{m}^2(\text{mg tot. chl } a)^{-1}$
$C_a$	Concentration of total chlorophyll $a$ (i.e. sum of chlorophylls $a$ + pheo derived spectrophotometrically)	$\text{mg tot. chl } a \text{ m}^{-3}$
$f_a, f_{\text{fl}, a}$	Non-photosynthetic pigment absorption factor	dimensionless
$f_{\text{fl}}, f_{\text{fl}, \Delta}$	Inefficiency factor in energy transfer and charge recombination	dimensionless
$f_{c(C_a(0))}, f_{\text{fl}, c(C_a(0))}$	Factor describing the effect of surface chlorophyll $a$ concentration on the portion of functional PS2 RC for photosynthesis and fluorescence respectively	dimensionless
$f_{\text{fl}, c(\text{PAR}_{\text{inh}})}$	Factors describing the reduction in the portion of functional PS2 RC as a result of photoinhibition	dimensionless
$f_{E, t}$	Classic dependence of photosynthesis on light and temperature also known as the light curve of photosynthesis efficiency at a given temperature	dimensionless
$f_{\text{fl}, E, t}$	Factor describing the effect of irradiance and temperature on phytoplankton fluorescence	dimensionless
$F_0$	Constant fluorescence	arbitrary units
$F_v$	Variable fluorescence	arbitrary units
PS2 RC	Reaction Centre in photosynthetic apparatus	
PAR	Photosynthetically Available Radiation	

**List of the abbreviations and symbols used in the text** (*continued*)

1	2	3
$PAR$	Downward irradiance in the PAR spectral range (400–700 nm)	$\mu\text{Ein m}^{-2} \text{ s}^{-1}$
$PAR(0)$	Downward irradiance in the PAR spectral range (400–700 nm) just below the surface	$\mu\text{Ein m}^{-2} \text{ s}^{-1}$
$PUR_{PSP}^*$	Number of quanta absorbed by photosynthetic pigments in unit time referred to unit mass of chlorophyll <i>a</i>	$\mu\text{Ein (mg tot. chl } a)^{-1} \text{ s}^{-1}$
SICF	Sun-Induced Chlorophyll <i>a</i> Fluorescence	
$temp$	Ambient water temperature	$^{\circ}\text{C}$
$z$	Real depths in the sea	m
$\tau$	Optical depth in the sea	dimensionless
$\lambda$	Wavelength of the light	nm
$\Phi_{ph}$	Quantum yield of photosynthesis	mol atC Ein <sup>-1</sup> or molC Ein <sup>-1</sup>
$\Phi_{fl}$	Quantum yield of fluorescence	Ein Ein <sup>-1</sup> i.e. dimensionless
$\Phi_{fl,0}$	Quantum yield of fluorescence, associated with the constant fluorescence $F_0$	Ein Ein <sup>-1</sup> i.e. dimensionless
$\Phi_{fl,v}$	Quantum yield of fluorescence, associated with the variable fluorescence $F_v$	Ein Ein <sup>-1</sup> i.e. dimensionless
$\Phi_H$	Quantum yield of direct heat production, i.e. the nonphotochemical radiationless dissipation of the excitation energy of pigments	Ein Ein <sup>-1</sup> i.e. dimensionless
$\Phi_{ph,MAX}$	Theoretical maximum possible quantum yield of photosynthesis	atomC quanta <sup>-1</sup> or molC Ein <sup>-1</sup>
$\Phi_{fl,v,MAX}$	Theoretical maximum possible quantum yield of fluorescence	Ein Ein <sup>-1</sup> i.e. dimensionless