Communications

Modified relationships between the occurrence of photoprotecting carotenoids of phytoplankton and Potentially Destructive Radiation in the sea

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ROMAN MAJCHROWSKI Institute of Physics, Pedagogical University, Arciszewskiego 22 B, 76–200 Słupsk, Poland;

e-mail: roman@wsp.slupsk.pl

MIROSŁAWA OSTROWSKA Institute of Oceanology, Polish Academy of Sciences, Powstańców Warszawy 55, 81–712 Sopot, Poland

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Abstract

The paper analyses the statistical relationships between photoprotecting pigment concentrations (principally selected groups of carotenoids), chlorophyll *a* concentrations and absolute values of the natural irradiance in the sea. The data from 404 sites in various regions (the authors' own investigations and data available on the Internet – about 3000 data sets altogether) were examined. This analysis confirms the close relationships between the occurrence of photoprotecting pigments and irradiance at short waves in the PAR range ($\lambda < 480$ nm). Modified statistical relationships between the relative concentration of photoprotecting pigments (ratio of photoprotecting pigments to total chlorophyll *a* concentration) and the Potentially Destructive Radiation (PDR^{*}) have therefore been elaborated. The latter is the quantity of irradiance from the short-wave PAR range absorbed per chlorophyll *a* mass unit.

The spectral light absorption capacity of phytoplankton depends on its pigment composition (Woźniak & Ostrowska 1990b, Bricaud *et al.* 1995, Woźniak *et al.* 1999). Diversity in pigment composition is caused by differences in the systematic groups of phytoplankton (Parsons et al. 1977, Jeffrey 1980, Claustre 1994) and the photo- and chromatic acclimation to light conditions (Woźniak & Ostrowska 1990a, Babin et al. 1996a, Babin et al. 1996b). Accessory pigments play different parts in the photosynthetic apparatus of plants. Most phytoplankton pigments (chlorophylls a, b, c, phycobilins and some carotenoids) transfer absorbed energy to chlorophyll and take a direct part in photosynthesis. Plants also contain photoprotecting pigments that protect the photosynthetic apparatus against photodestructive visible light from the short-wave range. It is well known that a molecule of chlorophyll a achieves the triplet state after excitation by a photon of sufficiently high energy (e.g. for $\lambda < 480$ nm). In this state it can be more easily destroyed by oxidation (Govindjee 1975). To avoid such a situation, plants produce protective pigments that absorb short-wave light, the so-called Photoprotecting Carotenoids (PPC) e.g. diadinoxanthin, alloxanthin, zeaxanthin, diatoxanthin, lutein, antheraxanthin, β -carotene, violaxanthin, neoxanthin, dinoxanthin (Bidigare *et al.* 1990). The energy absorbed by these pigments is not used for photosynthesis; that is to say, it is photosynthetically useless.

So when analysing the energy absorbed by phytoplankton with respect to its photosynthetic utility under natural conditions, it should be divided into photosynthetically useful and useless parts. The latter depends on the *PPC* content in phytoplankton, which varies in different seas and depths.

For a long time it was considered that PPC concentrations in phytoplankton are highest in the surface layer and decrease with depth *e.g.* Margalef (1967), Koblentz-Mishke (1971), Woźniak & Ostrowska (1990a). The experimental examples in Fig. 1 do indeed reflect that view. Such changes in the phytoplankton pigment composition can be explained by the photoacclimation strategy of natural phytoplankton communities. High intensities of potentially harmful short-wave irradiation in shallow waters cause PPC concentrations in the surface-layer phytoplankton to rise. However, the correlations between PPC content and real or optical depth are poor and cannot be used to quantitatively determine PPCconcentration.

Babin *et al.* (1996a,b) achieved some progress in the search for a quantitative factor governing PPC occurrence on the basis of investigations at eutrophic, mesotrophic and oligotrophic sites in the north-east Atlantic during the EUMELI experiment. They worked out a relationship between the non-photosynthetic pigment index (the ratio of PPC to the sum of all photosynthetic and photoprotecting phytoplankton pigments) and the mean daily PAR in the mixed layer (ibid. Fig. 12). However, their relationship



Fig. 1. Vertical profiles of typical photoprotecting carotenoids C_{PPC} to total chlorophyll *a* C_a ratio: for real depth -z (a); for optical depth $-\tau$ (b) recorded at the same stations with different surface total chlorophyll *a* concentrations $C_a(0) [\text{mg m}^{-3}];$

- O1 Polish-Russian database Pacific $(C_a(0) = 0.05 \,\mathrm{mg \, m^{-3}})$
- O2 tt011 Equator, Pacific $(C_a(0) = 0.072 \,\mathrm{mg \, m^{-3}})$
- O3 tt007 Equator, Pacific $(C_a(0) = 0.158 \,\mathrm{mg}\,\mathrm{m}^{-3})$
- M ttn-49 Arabian Sea $(C_a(0) = 0.341 \,\mathrm{mg \, m^{-3}})$
- P ttn-49 Arabian Sea $(C_a(0) = 0.794 \,\mathrm{mg \, m^{-3}})$
- E1 ttn-49 Arabian Sea $(C_a(0) = 1.38 \,\mathrm{mg \, m^{-3}})$
- E2 ttn-49 Arabian Sea $(C_a(0) = 2.42 \,\mathrm{mg \, m^{-3}})$
- E3 ULISSE Baltic Sea $(C_a(0) = 7.09 \,\mathrm{mg}\,\mathrm{m}^{-3})$

is not universal and cannot be used to make a precise quantitative determination of PPC concentration.

Significant progress in the search for the principal factors controlling the occurrence of PPC was achieved by Woźniak *et al.* (1997). They showed that the factor most intimately connected with the relative concentration of PPC, the C_{PPC}/C_a ratio, is the so-called potentially destructive radiation (PDR). By destructive radiation is meant the quantity of high-energy photons capable of bringing about the C_a triplet state and thereby increasing the probability of photo-oxidation. We define PDR as follows:

$$PDR^* = \int_{400}^{480} a_a^*(\lambda) < E(\lambda) >_{\text{day}} d\lambda, \tag{1}$$

where

 PDR^* – is the Potentially Destructive Radiation (the asterisk indicates that this is the PDR per unit of chlorophyll mass),

- $E(\lambda)$ the typical scalar irradiance level in the medium in this paper, its daily mean value $\langle E(\lambda) \rangle_{dav}$,
- a_a^* the specific absorption coefficient of chlorophyll *a*, determined from the sum of Gaussian bands (Woźniak *et al.* 1999).

It was established that the relative PPC concentration fell with decreasing PDR^* according to the relation

$$C_{PPC} = \left(0.5077 < PDR^* >^{0.3669}_{\Delta z = 10 \,\mathrm{m}}\right) C_a,\tag{2}$$

where the mean $< PDR^* >_{\Delta z=10\,\mathrm{m}}$ is the mean value in a water layer $\Delta z + \Delta z'$

$$< PDR^* >_{\Delta z=10 \,\mathrm{m}} = \frac{1}{\Delta z + \Delta z'} \int_{z-\Delta z'}^{z+\Delta z'} PDR^*(z) \, dz,$$
 (3)

$$\Delta z = 10 \,\mathrm{m} \quad \text{and} \quad \Delta z' = \begin{cases} z & \text{if } z < 10 \,\mathrm{m} \\ 10 \,\mathrm{m} & \text{if } z \ge 10 \,\mathrm{m} \end{cases} .$$
(4)

Therefore, the influence of water mixing was, very approximately, taken into consideration.

Formula 2 was obtained from poor experimental material (only 186 points). Our experience shows that it cannot be used to predict *PPC* concentrations under different conditions in the sea because of its considerable inherent inaccuracy.

The aim of the present work, therefore, is to modify the relationship between the occurrence of PPC and PDR^* on the basis of an enlarged database.

The material for our analyses was the empirical database constructed from our own investigations, the joint Polish-Russian database, and the data available on the Internet – the U.S. JGOFS Data System (Table 1).

Our database included the sets of empirical data on

- phytoplankton pigment concentrations (different types of chlorophylls and carotenoids) determined by a variety of chromatic methods, mainly by HPLC (High Performance Liquid Chromatography) or, in the nineteen-sixties and early seventies, by TLC (Thin Layer Chromatography);
- spectral light distributions at different depths in the sea.

The direct measurements of the spectral light distribution at different depths in the sea were carried out only for the Polish-Russian database

Fxneriment	Stations	Sets of	Location	References, or author of	Ontical me	asurements
		measure- ments		measurements C_a and C_{PPC}	at surface	at different depths
1	2	3	4	5	9	2
Polish-Russian database	46	219	Baltic, Black Sea, Pacific	Koblentz-Mishke & Semenova (1975), Kornushenko <i>et al.</i> (1980)	+	+
ULISSE	30	82	Baltic	Olaizola (1996)	+	+
U.S. JGOFS DS EqPac tt007	39	419	Pacific – Equator	Bidigare (1992a)	+ Newton (1992a)	I
U.S. JGOFS DS EqPac tt008	33	234	Pacific – Equator	Bidigare (1992b)	2 sites Newton (1992b)	I
U.S. JGOFS DS EqPac tt011	44	475	Pacific – Equator	Bidigare (1992c)	38 sites Newton (1992c)	I
U.S. JGOFS DS EqPac tt012	34	215	Pacific – Equator	Bidigare (1992d)	1	I
U.S. JGOFS DS Arabian ttn-43	77	530	Arabian Sea	Goericke (1995a)	I	I
U.S. JGOFS DS Arabian ttn-45	29	255	Arabian Sea	Bidigare (1995)	I	I
U.S. JGOFS DS Arabian ttn-49	72	505	Arabian Sea	Goericke (1995b)	Ι	I
total	404	2934				

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and during the ULISSE¹ experiment, for 76 of 404 stations analysed – Table 1, columns 6 and 7. Unfortunately, in the other cases (328 stations), only the total irradiance at the sea surface was measured and/or optical measurements in the sea were carried out sporadically. In such situations, if the relevant optical measurements at the surface are unavailable, the typical surface spectral PAR irradiance is assumed for each geographical zone (Timofieyev 1983). On the other hand, the missing underwater light field distributions in different trophic types of seas were estimated according to the algorithm in Woźniak *et al.* (1992). This algorithm is based on the bio-optical model of the relation between the spectral irradiance attenuation coefficient and the concentration of chlorophyll *a* in the sea. The accuracy of these estimations seems to be satisfactory: the errors of such estimations with reference to underwater irradiation attenuation coefficients are of the order of 10% (see Woźniak *et al.* 1992).

The following parameters were determined on the basis of this input data as material for statistical analyses:

- 1) the relative PPC concentration, defined as the ratio C_{PPC}/C_a , where C_a denotes the sum of chl *a* and divinyl chl *a* at different depths in the sea;
- PDR* values typical of these depths determined from eq. (1) using the specific light absorption coefficient spectra of chlorophyll a according to Woźniak et al. (1999).

About 3000 points of the C_{PPC}/C_a , vs PDR^* relationship at different depths in the sea were examined altogether.

The analysis shows that PPC concentrations depend to a lesser degree solely on optical depth or the absolute level of total PAR irradiance. There is, however, a close link between the PPC concentration and the absolute PDR^* level. The latter relationships were examined, taking into consideration mean values of PDR^* in water layers of different thickness Δz (see eq. (4)).

The correlation for the $C_{PPC}/C_a vs PDR^*$ dependence was highest for $\Delta z \approx 30 \text{ m}, i.e.$

$$\Delta z = 30 \,\mathrm{m} \quad \text{and} \quad \Delta z' = \begin{cases} z & \text{if } z < 30 \,\mathrm{m} \\ 30 \,\mathrm{m} & \text{if } z \ge 30 \,\mathrm{m} \end{cases}.$$
(5)

¹Underwater Light Seatruth Satellite Experiment, in co-operation with the Commission of the European Union Joint Research Centre, Ispra, Italy and the Institute of Oceanology PAS (Ooms 1996).



Fig. 2. Statistical dependence of photoprotecting carotenoids C - PPC to total chlorophyll *a* C_a ratio on the mean Potentially Destructive Radiation $\langle PDR^* \rangle_{\Delta z=30 \text{ m}}$ (dots – measured, line – calculated from eq. (6))

	Arithmetic statistics		Logarithmic statistics			
	systematic	statistical	systematic	range of	variability	variability factor
	$\langle \varepsilon \rangle$ [%]	$\sigma_{arepsilon}$ [%]	$\langle \varepsilon \rangle_g ~[\%]$	σ_{-} [%]	$\sigma_+ \ [\%]$	x
Woźniak <i>et al.</i> (1997), eq. (2)	-8.71	± 53.96	-23.35	-58.94	43.08	1.87
modified by us eq. (6)	7.80	± 45.02	-0.22	-32.35	47.16	1.47

Table 2. The relative errors in estimating PDR^* from two formulas

where

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

 σ_{ε} – standard deviation of errors (statistical error),

 $\langle \varepsilon \rangle_q = 10^{[\langle \log(C_{PPC, C}/C_{PPC, M}) \rangle]} - 1$ – geometric mean of errors,

$$\sigma_{-} = 10^{\left[\left\langle \log(C_{PPC, C}/C_{PPC, M}) \right\rangle - \sigma_{\log} \right]} - 1 \quad \text{and}$$

 $\sigma_{+} = 10^{[\langle \log(C_{PPC, C}/C_{PPC, M})\rangle + \sigma_{\log}]} - 1,$

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

 σ_{\log} – standard deviation of $\log(C_{PPC, C}/C_{PPC, M})$,

 $< \log(C_{PPC,C}/C_{PPC,M}) > -$ mean of $\log(C_{PPC,C}/C_{PPC,M})$.

The following modified relationship describing the relative PPC concentration as a function of $\langle PDR^* \rangle_{\Delta z=30 \text{ m}}$ was found:

$$C_{PPC} = \left(0.1758 \ < PDR^* >_{\Delta z = 30 \,\mathrm{m}} + 0.1760\right) C_a. \tag{6}$$

Figure 2 compares the functional form of eq. (6) with the experimental points.

To estimate the errors, the measured PPC concentrations $(C_{PPC, M})$ were compared with the PPC concentrations calculated from eq. (6) on the basis of known C_a and PDR^* $(C_{PPC,C})$ (Figs. 3a and 3b). Figs. 3c and 3d



Fig. 3. Comparison between calculated and measured photoprotecting carotenoid concentrations and frequency distribution of the ratio $C_{PPC, C}/C_{PPC, M}$: (a) and (b) – for the relation in Woźniak *et al.* (1997) (eq. (2)); (c) and (d) – for the relation established in this paper (eq. (6))

make such a comparison for the relationship according to Woźniak *et al.* (1999) (see eq. (2)). Clearly, the accuracy of the relationship worked out in the present paper is a significant improvement as regards predicting *PPC* concentration from C_a concentration and optical characteristics. A variability factor 1.87 used to be regarded as suitable; now this value has decreased to 1.47 (see Table 2). Presumably, if direct measurements were used rather than estimations of underwater light fields to determine the relationship between *PPC* concentrations and *PDR*^{*}, the variability factor could be even better.

The attempt to find this mathematical relationship $(PPC/C_a vs PDR^*)$ with a non-linear function did not yield any significant improvement. Moreover, the physical significance of the linear model is much clearer. The constant term in eq. (6) is assumed to be the constant (background) concentration of PPC, independent of PDR^* . The remainder of the equation describes the linear increase in PPC concentration with increasing PDR^* . This means that PDR^* is the direct energy factor governing the quantity of photoprotecting pigments produced by a plant.

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Appendix 1

Notation

Symbol	Denotes	Units
a_a^*	specific light absorption coefficient of chlorophylls a in solvent	$m^2 (mg \text{ tot. chl } a)^{-1}$
C_a	sum of chlorophylls a + pheo, or total chlorophyll (chl a + divinyl chl a) concentrations	mg tot. chl $a~{\rm m}^{-3}$
$C_{PPC},$	concentrations of photoprotecting carotenoids	mg pigment m^{-3}
PAR	photosynthetically available radiation	
PPC	photoprotecting carotenoids	
z	depth in the sea	m
λ	light wavelength	nm
PDR^*	potentially destructive radiation (per unit of chlorophyll a mass)	$\mu \mathrm{Ein}(\mathrm{mg}\mathrm{chl}a)^{-1}\mathrm{s}^{-1}$
$< PDR^* >_{\Delta z = 10 \mathrm{m}}$	mean PDR^* value in a 10 m-deep water layer	$\mu \mathrm{Ein}(\mathrm{mg} \mathrm{chl}\; a)^{-1}\mathrm{s}^{-1}$
$< PDR^* >_{\Delta z = 30\mathrm{m}}$	mean PDR^* value in a 30 m-deep water layer	$\mu \mathrm{Ein}(\mathrm{mg} \operatorname{chl} a)^{-1}\mathrm{s}^{-1}$
$\Delta z, \Delta z'$	thicknesses of water layers	m
$E(\lambda)$	spectral scalar irradiance	$\mu {\rm Ein}{\rm m}^{-2}{\rm s}^{-1}{\rm nm}^{-1}$