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LIGHT ABSORPTION AND MAXIMUM QUANTUM YIELD OF PHOTOSYNTHESIS DURING AUTUMN PHYTOPLANKTON BLOOM IN THE WESTERN BLACK SEA

In the frame of GEF/UNDP Black Sea Ecosystem Recovery Project the effect of nutrient availability on phytoplankton light absorption and maximum quantum yield of carbon fixation (ϕ_{max}) has been investigated. It has been found out that chlorophyll *a* concentration (Chl *a*) varied from 0.3 to 10 mg m^{-3} increasing from deep-water region to shelf waters. At the shallow stations, where upper mixed layer spread deeper the bottom of euphotic zone, the homogenous pigment distribution was observed. In the deep-water region the Chl *a* profiles showed the presence of a deep Chl *a* maximum (DCM) below a seasonal density cline. The functional characteristics of phytoplankton showed depth-dependent variation. The phytoplankton from DCM was characterized 20 % lower values of spectral averaged Chl-*a* – specific light absorption $\overline{a}^{*}_{ph}$ (0.016±0.0025 m^2 $(mgChl)^{-1}$) and more than in two times higher values of ϕ_{max} (0.070±0.012 molC (mol quanta)$^{-1}$) compared with the surface phytoplankton $\overline{a}^{*}_{ph}$ (0.021±0.0035 m^2 $(mgChl)^{-1}$) and ϕ_{max} (0.030±0.0078 molC (mol quanta)$^{-1}$). From offshore to shallow stations the increasing of surface Chl *a* concentration was accompanied with slight decrease of $\overline{a}^{*}_{ph}$ (on ~20 %) and significant increase of ϕ_{max} up to its theoretical limit - 0.1 molC (mol quanta)$^{-1}$, which were caused by an increase in nutrient supply across the shelf.

Key words: Chlorophyll *a*, phytoplankton, light absorption, maximum quantum yield, nutrients.

Productivity in the Black Sea is known to vary strong in time and space, what is caused by variation in the main environmental factors such as nutrients, radiance and temperature. The spatial productivity heterogeneity is related to a difference in nutritional status between shelf and deep-waters, which is more pronounced in the western part of the sea. The productivity values in the north-western shelf waters differ on three orders from deep-water region because of the input of nutrients by three big rivers flowing in. It results in that a strong nutrient gradient is observed in the direction from offshore to shore zones [7]. Waters nutrient status controls intracellular pigment concentration, relative abundance of accessory light harvesting pigments and phytoplankton taxonomic and size structure, consequently, the nutrient concentrations effects on phytoplankton chlorophyll *a* – specific absorption [1, 25]. The maximum quantum yield of photosynthesis depends on nutrient concentration [1, 5], because the photochemical activity of photosystem reaction centers is depressed by nutrient limitation [11, 28]. The Chl *a* – specific absorption coefficient and especially maximum quantum yield of photosynthesis are found to be more sensitive to nutrients and could be the indicators of physiological state of phytoplankton community. However, for the Black Sea there are rather limited amount of maximum quantum yield of photosynthesis measurements. Only using of recent-day method of phytoplankton absorption measurement [3, 4] allowed to quantum yield estimation from efficiency of photosynthesis (initial slope of photosynthesis light –

curve) [9]. Two-year monitoring of bio-optical characteristics of surface layer in central western part of the Black Sea showed a relationship of absorption coefficients with chlorophyll *a* concentrations and revealed seasonal variability in chl*a*-specific phytoplankton absorption coefficients [4]. The depth-dependent variability in phytoplankton absorption features and its relationships with nutrient concentrations have not been still investigated, although such data would be important for estimation of physiological characteristic within euphotic zone.

The investigation aimed to estimate the variability in phytoplankton light absorption coefficient and maximum quantum yield of photosynthesis during the autumn phytoplankton bloom and their relationships with nutrient availability.

Methods. The investigation of pigment concentration, photosynthesis-irradiance relationships (P-E) and phytoplankton light absorption (a_{ph}) were curried out on a few cross shelf transects from Ukrainian, Bulgarian, Rumanian and Turkish coasts to the deep-waters region (Fig. 1) from 20 September to 15 October 2005 during a cruise on R/V "Vladimir Parshin". Sampling was generally performed at from dawn to midday.

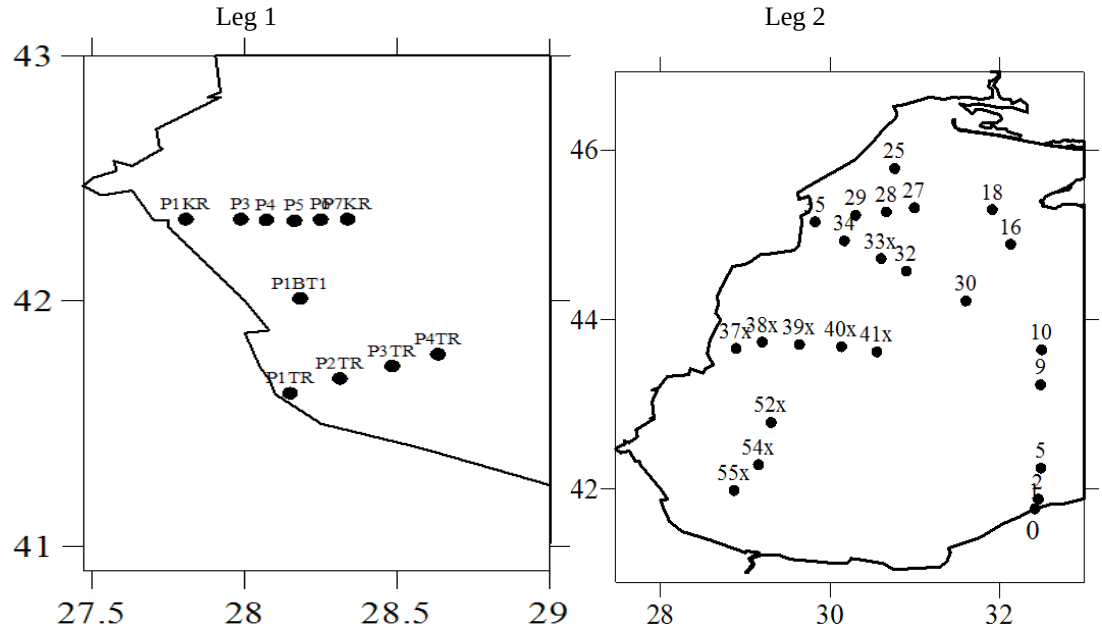

Fig. 1 Location of the biological stations in September (Leg 1) and October 2005 (Leg 2)
Рис. 1 Схема биологических станций в сентябре (этап 1) и октябре 2005 (этап 2)

Pigment concentrations. The sampling for pigment concentrations and light absorption measurements were done at 39 stations shown on scheme of stations (Fig. 1). Chl *a* and Phaeo concentrations were analyzed by the fluorometric method [13]. The fluorometer was calibrated using solution of purified chlorophyll *a* (Chl *a*) which concentrations were determined with spectrophotometer using the equations recommended by [14]. Water samples for pigment measurements were collected using 5-L bottles of CTD cassette at the 7 – 10 depths chosen based on a fluorescence profile to describe correctly vertical pigment distribution. Water samples (0.2 – 0.5 L) were gently filtered on 25 mm Whatman GF/F filters under ~0.2 atm. vacuum. Filters were folded in half twice and wrapped in aluminum foil, labeled, and stored in liquid nitrogen (to avoid formation of degradation

products) until shore analysis. After removal from liquid nitrogen, the pigments were extracted by placing the filters in 5.0 ml 90 % acetone. The samples were allowed to extract overnight in 90 % acetone in the dark refrigerator (~ 6°C). The samples were vortexed to break cell walls, and spun down in a centrifuge for 5 min to remove cellular debris and glass fibers and then measured before and after acidification. The sample was acidified with 2 drops of 1.2 M HCl. All procedures were conducted under subdued light in order to prevent photodegradation of pigments.

Particulate and phytoplankton light absorption. The sample processing was performed respecting the ocean optics protocols recommended for satellite ocean color sensor validation [6]. Water samples (0.5 – 1.0 L) were gently filtered on 25 mm Whatman GF/F filters under ~0.2 atm. vacuum. Filters were placed in special plastic capsule and then stored in liquid nitrogen until analysis in the laboratory. The particulate absorption was measured by method [27] in modification [21]. The optical density of the filters was measured relatively to a seawater reference saturated blank filter with dual beam spectrophotometer (SPECORD-M40, Carl Zeis Yena). All spectra were offset to zero optical density at 750 nm, and corrected for the path-length amplification effects as described in [20]. The total particle absorption ($a_p(\lambda)$) was separated into phytoplankton ($a_{ph}(\lambda)$) and non-algal particles absorption ($a_{NAP}(\lambda)$) by the methanol extraction method [15]. The measurement made before methanol extraction provided $a_p(\lambda)$ while $a_{NAP}(\lambda)$ was obtained after the extraction. $a_{ph}(\lambda)$ was derived from the difference between $a_p(\lambda)$ and $a_{NAP}(\lambda)$. To calculate Chl *a*-specific coefficient ($a^*_{ph}(\lambda)$) phytoplankton absorption coefficient $a_{ph}(\lambda)$ was divided by a sum of Chl *a* concentration with phaeopigment concentration (TChl *a*).

Maximum quantum yield of carbon fixation. The photosynthesis – irradiance (P-I) curves and phytoplankton light absorption spectra were used to calculate maximum quantum yield of carbon fixation (ϕ_{max}). P-I experiments were carried out at 23 stations (23 experiments – for surface samples (where photosynthetic available radiance, PAR = 100%) and 7 ones - for deep samples (~1 % PAR). The depths to which 1 % of surface irradiance penetrated were determined based on PAR profile measured by PAR sensor attached to CTD-rosette. The method of P-I curve measurements and the results were described in [9].

The maximum quantum yield of carbon fixation (ϕ_{max}) was determined by the formula:

$$\phi_{max} = k\,\alpha^B / \bar{a}_{ph}, \qquad (1)$$

where α^B is the efficiency of photosynthesis, normalized to unity of Chl *a* concentration (initial slope of P-I curve); k is the coefficient for dimensional consistency of this equation, $\bar{a}_{ph}$ is the amount of absorbed quanta, which is normalized to unity of incident quanta in visible diapason of wavelengths from 400 to 700 nm (photosynthetically available radiation):

$$\bar{a}_{ph} = \frac{\int_{400}^{700} a_{ph}(\lambda)d\lambda \times Q(\lambda)d\lambda}{\int_{400}^{700} Q(\lambda)d\lambda} \qquad (2)$$

Spectral distribution of the light energy in the experiments ($Q(\lambda)$) was determined as the product of the energy spectrum of the lamp ($E_L(\lambda)$) and light transmission spectrum of 10 % water solution of $CuSO_4$ - $T(\lambda)$:

$$Q(\lambda) = E_L(\lambda) \times T(\lambda) \qquad (3)$$

Nutrient concentration. Nitrate, nitrite, phosphate, and silicate concentration were measured on the board of R/V "Vladimir Parshin" just after the sampling with the autoanalyser by the standard techniques [26].

Results and discussion. The surface chlorophyll a concentrations varied from 0.3 to 10 mg m^{-3} increasing from deep-water region to shelf waters. Vertical chlorophyll *a* profiles were obtained based on fluorescence profiles and

correlation between chlorophyll *a* concentration and fluorescence of chlorophyll *a (*Flu*)*:

Chl = 0.00154×Flu, n=101, r^2= 0.92 (4)

The chlorophyll *a* concentration, phytoplankton absorption coefficient ($a_{ph}(\lambda)$) and maximum quantum yield of photosynthesis (ϕ_{max}) varied in a wide range along the transects from offshore to shore regions and with depths.

Depth-dependent variation of $a_{ph}(\lambda)$ and ϕ_{max} in deep-waters region. In the investigated area euphotic zone was deeper than mixed upper layer. Photosynthetically available radiance attenuated up to 1 % of surface PAR value within 35 – 58 m layer (Fig. 2). Seasonal density stratification located at 14 – 22 m depth (Fig. 2).

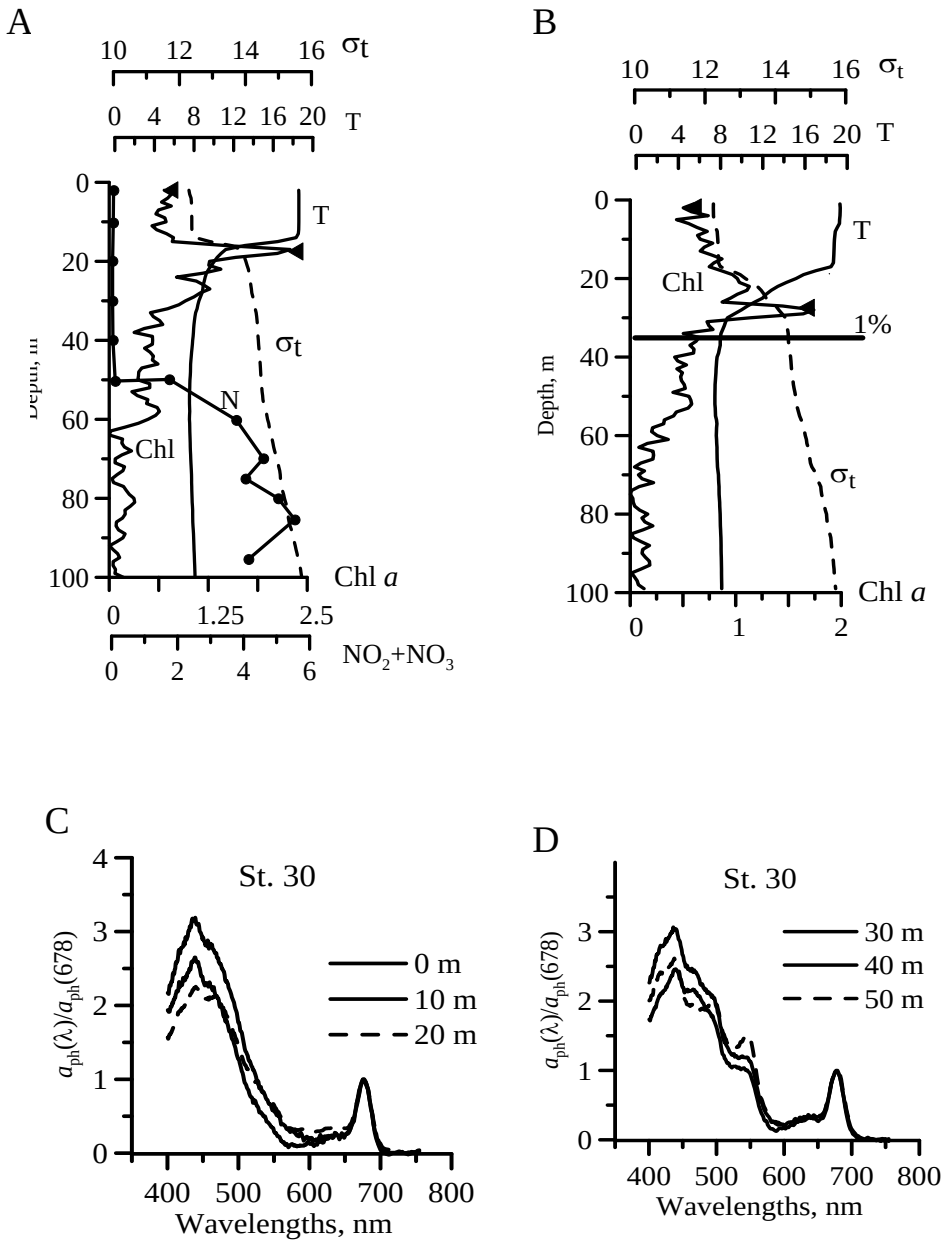

Fig. 2 Typical for the deep-waters region vertical profiles of chlorophyll *a* concentration (Chl *a*, mg m^{-3}), temperature (T, ^{0}C), nitrate and nitrite concentration (NO_3+NO_2, μM) and relative density (σ_t, kg m^{-3}) – A, B (Horizontal line shows depth of 1% PAR, ▲ – the depths of P-I experiments); Phytoplankton absorption spectra, normalized on coefficient at 678 nm ($a_{ph}(\lambda)$/ $a_{ph}(678)$) – C, D.

Рис. 2 Типичное для глубоководного района вертикальное распределение концентрации хлорофилла *a* (Chl *a*, мг $м^{-3}$), температуры (T, ^{0}C), концентрации нитратов и нитритов (NO_3+NO_2, μM) и относительной плотности (σ_t, кг $м^{-3}$) (Горизонтальной линией отмечена глубина 1% ФАР, ▲ – глубины экспериментов по определению световых зависимостей фотосинтеза) – A, B; Спектры поглощения света фитопланктоном, нормализованные на величину при 678 нм ($a_{ph}(\lambda)/a_{ph}(678)$) – C, D.

The stratification was found not to be strong, which was typical for autumn. The maximum density gradient was equal 0.03 – 0.06 (kg m^{-3}) m^{-1}. The density-cline divided the euphotic

zone into two quasi-isolated layers with different environmental factors. Upper mixed layer was characterized by higher temperature and light intensity than the layer below the thermo-cline. It resulted in pronounced depth dependent variability in phytoplankton pigment concentrations and light phytoplankton absorption spectra shapes within the euphotic zone. The surface Chl *a* concentration varied from 0.33 to 0.85 mg m^{-3}. In the upper mixed layer the Chl *a* concentration distribution was rather uniform. In the deeper layer located below the seasonal density cline Chl *a* maximum was observed (Fig. 2).

To estimate spectra shape variation the absorption spectra were normalized to red peak absorption value. The phytoplankton light absorption within the upper mixed layer was characterized by identical spectra shapes (Fig. 2C, 2D). The spectral distribution of absorption coefficient depends on phytoplankton pigment composition [24]. Therefore similarity in spectra shape reflects that pigment composition was similar within the mixed layer and the species composition and cell size structure of phytoplankton community is unlikely to vary within this layer. In the deeper (30 – 60 m) layer the shape of absorption spectra markedly changed (Fig. 2C, 2D). Near the bottom of euphotic zone in the absorption spectra local maximum at ~ 550 nm became visible. It is well known that this capability to absorb green wavelengths (~550 nm; Fig. 2C, 2D) is owing to phycobilins, which are pigments – markers of cyanobacteria [22]. The domination of cyanobacteria in phytoplankton in the layer below the seasonal thermo-cline seems to be reasonable. Within the euphotic zone spectral features of irradiance change with depth, and mainly green light penetrates down to the euphotic zone bottom [19]. Cyanobacteria due to the phycobilins absorb more effectively green light than other taxons.

Chl-*a* specific absorption coefficients ($a^*_{ph}(\lambda)$) decreased with depth, especially in the blue part of spectrum. It resulted in the decrease of blue (at 438 nm) to red (at 678 nm) peak ratio, R (Fig. 2C, 2D). The mean values of $a^*_{ph}(678)$ and R varied from 0.0181 (±15%) m^2 (mg Chl)$^{-1}$ and 2.7 (±17%) at the surface to 0.0172 (±14%) m^2 (mg Chl)$^{-1}$ and 2.15 (±10%) at the 1% PAR depth (Table 1).

As result of variation in both specific absorption coefficient and spectrum shape the spectrally averaged Chl *a* – specific coefficient ($\overline{a}^*_{ph}$), decreased within the euphotic zone from 0.0205 (±20 %) to 0.0157 (±21 %) m^2 (mg Chl)$^{-1}$.

Parameters	Surface (n=7)	1 – 5 % PAR (n=8)
Chl *a*	0.55 (± 31%)	1.4 (± 85%)
$a^*_{ph}(678)$	0.0181 (± 15%)	0.0172 (± 14%)
R	2.70 (± 17%)	2.15 (± 10%)
$\overline{a}^*_{ph}$	0.0205 (± 20%)	0.0157 (± 21%)
ϕ_{max}	0.030 (± 26%)	0.070 (± 18%)

Table 1 Mean values and standard deviation (in a bracket) of some biooptical parameters in the deep-waters region.

Табл. 1 Среднее значение и стандартное отклонение (в скобках) биооптических параметров в глубоководной части моря

Comments: Chl *a* - chlorophyll *a* concentration, mg m^{-3}; $a^*_{ph}(678)$ - chlorophyll *a* - specific absorption coefficient at red peak, m^2 (mgChl)$^{-1}$; R - blue to red peaks ratio in absorption spectra; $\overline{a}^*_{ph}$ - spectrally averaged chlorophyll a-specific coefficient, m^2 (mg Chl)$^{-1}$ and ϕ_{max} - maxim quantum yield of carbon fixation, mol C (mol quanta)$^{-1}$

Примечание: Chl *a* - концентрация хлорофилла *a,* мг $м^{-3}$; $a^*_{ph}(678)$ - нормированный на хлорофилл *a* коэффициент поглощения света фитопланктоном в красном максимуме, $м^2$ (мгChl)$^{-1}$; R – отношение коэффициентов поглощения в синем и красном максимумах; $\overline{a}^*_{ph}$ - средняя по спектру величина нормированного на хлорофилл *a* коэффициента поглощения света фитопланктоном, $м^2$ (мгChl)$^{-1}$ и ϕ_{max} – максимальный квантовый выход фотосинтеза, мольС (моль квантов)$^{-1}$

Chl *a*- specific absorption coefficients decreased slightly with depth within the euphotic layer. It could be explained by low pigment packaging degree in phytoplankton cells of surface layer and relatively high Chl *a*- specific coefficients at the bottom of euphotic zone due to domination of cyanobacteria, which is known [22] to be characterized by relatively high $a^*_{ph}(\lambda)$ in blue part of spectrum due to higher accessory pigment to Chl *a* ratio than in other phytoplankton taxon groups. The variations in $a^*_{ph}(\lambda)$ values are caused pigment composition and intracellular pigment packaging [23]. Recent investigations [2, 17] showed that package effects were responsible for up to a 62 % reduction in the chl*a*-specific absorption coefficients at the blue part of spectra, particularly for populations dominated by larger phytoplankton. On the other hand variations in pigment composition due to change of phytoplankton taxonomic structure were also found to have smaller impact (10 – 28 %) on variations in total absorption.

The pigment packaging degree is well known to depend on intracellular pigment concentration and cell size [23]. The pigment concentration in cells is changed to acclimate to main environmental factors as irradiance, nutrients and temperature. The physiological acclimation of planktonic algae to a decrease of irradiance and to an increase of nutrients concentration is accompanied with an increasing of intracellular chlorophyll to organic carbon ratio [10], which results in reduction of $a^*_{ph}(\lambda)$ values. The size-dependence of absorption was shown to be a pronounced characteristic of phytoplankton under low light conditions, but under high light conditions, size-dependence of absorption at 440 nm weakens due to the effects of absorption by photoprotective pigments in the blue region of the spectrum [11]. These results explain what might cause the rather vertical homogeneity in $a^*_{ph}(\lambda)$ obtained in our study.

This vertical stability of $a^*_{ph}(\lambda)$ allowed combining data from all depths to get relationships between light absorption coefficients and TChl *a* concentrations described by power functions: for the blue peak

$$a_{ph}(440) = 0.0451\ x^{0.94},\ n=39,\ r^2=0.83 \qquad (5)$$

and for the red peak

$$a_{ph}(678) = 0.0181\ x^{0.92},\ n=39,\ r^2=0.91 \qquad (6)$$

High values of power coefficients (close to 1) show, that Chl*a*-specific coefficients were practically constant for that range of pigment concentrations (from 0.16 to 2.3 mg m^{-3}). The obtained relationships differ (by higher power coefficients) from results of two years long monitoring of surface phytoplankton absorption characteristics [4]. During that bio-optical monitoring the chlorophyll concentration reached maximum (about 2 mg m^{-3}) in winter-spring bloom of diatoms. The difference in power coefficients is likely to reflect the seasonal variations in chl*a*-specific absorptions due to package effect resulted from photo physiological response of phytoplankton to different environmental factors.

The maximum quantum yield of carbon fixation increased significantly with depth in stratified waters from 0.030 (±26 %) to 0.070 (±18 %) molC (mol quanta)$^{-1}$ on average (Table 1). The phytoplankton near the bottom of euphotic zone (~ 1% PAR) acclimated to ambient environmental conditions was characterized by ϕ_{max} values closed to upper theoretical limits of photosynthesis quantum yield (0.1 molC (mol quanta)$^{-1}$).

The low values of ϕ_{max} in the surface layer are caused by the high phytoplankton pigment absorbance in blue part of spectra, which could be related with the presence of pigments-photoprotectors. The ϕ_{max} co-varied with depth at the oligothrophic site in Ocean and decreased with increasing of relative concentrations of non-photosynthetic pigments [1]. In that study was shown that the variable contribution of non-phototsynthetic absorption could explain 3-fold variation in the ϕ_{max}. At the same time nutrients

availability factor was responsible for 2-fold variation in the ϕ_{max} [1]. In our study the ϕ_{max} was determined as an assimilation of organic carbon divided by photons absorbed by all pigments including both photosynthetic and photoprotective pigments. The spectral averaged absorption coefficient decreased from surface to the bottom of the euphotic zone on 20 % (Table 1). This decreasing could be caused by both reduction relative content of accessory pigments (including photoprotective pigments) and increasing of pigment packaging degree. The contribution of absorption changing to the depth-dependent ϕ_{max} variation was equal ~ 20%. Consequently, a 2-fold variation (80 % of total 2.3-fold variation) in the ϕ_{max} could be caused by an effect of ambient environmental factors namely nutrient concentration and light intensity. Laboratory studies on quantum efficiency of photosynthesis of planktonic algae cultures demonstrated that nutrient stress can markedly reduce an activity of photosystem reaction center and consequently ϕ_{max} [5, 16]. Value of ϕ_{max} declines at high irradiance in nutrient-replete cultures, because of the increasing of photoprotective pigments contribution to total absorption [18]. In our study high incident solar radiation and nutrients limitation (occurred in subsurface layer) could effect the photochemistry efficiency reaction centers and subsequently decrease ϕ_{max}. Obtained results that near the bottom of euphotic zone phytoplankton utilized the absorbed photons with yield closed to its potential maximum value allow making a conclusion about high nutrient availability of phytoplankton in this deep water layer. For this deep water layer the correlation between ϕ_{max} and nitrate concentrations was not revealed. But values of ϕ_{max} decreased with increasing of a distance to the depth with maximum gradient of nitrate concentrations. This distance indirectly characterizes dynamics of nutrient upflow from nitro-cline to the deep layer of euphotic zone. Consequently, for the deeper phytoplankton (below the seasonal thermocline) maximum quantum yield of carbon fixation was rather high and depended on nutrient availability namely - dynamics of nutrient upflow.

Variation of a_{ph} and ϕ_{max} along transects across the shelf. In the shore zone in contrast to the deep-waters region the euphotic zone was equal or shallower than the mixed layer. In the shelf waters the euphotic zone was in a range 15-55m in opposite relation to surface Chl *a* concentration. The mixed layer was characterized rather uniform distribution of pigment concentrations and similar shape of absorption spectra (Fig. 3), which are caused by an intensive mixing in autumn. It is suggested to be accompanied with homogenous phytoplankton distributions. In the shelf waters the P-I experiments were done generally from the surface samples and only at two stations from depths near the bottom of euphotic zone. The character of changing ϕ_{max} values with depths was different. On the station 2 ϕ_{max} increased from (0.027 to 0.069 molC (mol quanta)$^{-1}$), but on the other station (st.16) ϕ_{max} value at the surface was relatively high and close to those for deep phytoplankton (0.073 and 0.063 molC (mol quanta)$^{-1}$) (Fig. 3). This difference is likely to be related with different size structure of surface phytoplankton community, because nutrient availability was the same.

The mean values of the parameters for the stations where P-I experiments were carried out (Table 2) showed that in the shelf waters Chl *a* concentration and ϕ_{max} were higher (2.6 ±74% m^2 (mgChl)$^{-1}$ and 0.049±68% mol C (mol quanta)$^{-1}$), but light absorption characteristics $a^*_{ph}(678)$, $\overline{a}^*_{ph}$ and R were lower (0.0164±17%, 0.0158 ±21% m^2 (mgChl)$^{-1}$ and 2.31±17 %) compared to deep-waters parameters. The high standard deviations obtained for Chl *a* concentrations (±74 %) and for ϕ_{max} (±68 %) reflects that these parameters were more variable increasing across the shelf and they could characterize the physiological heterogeneity of phytoplankton community (Fig. 4).

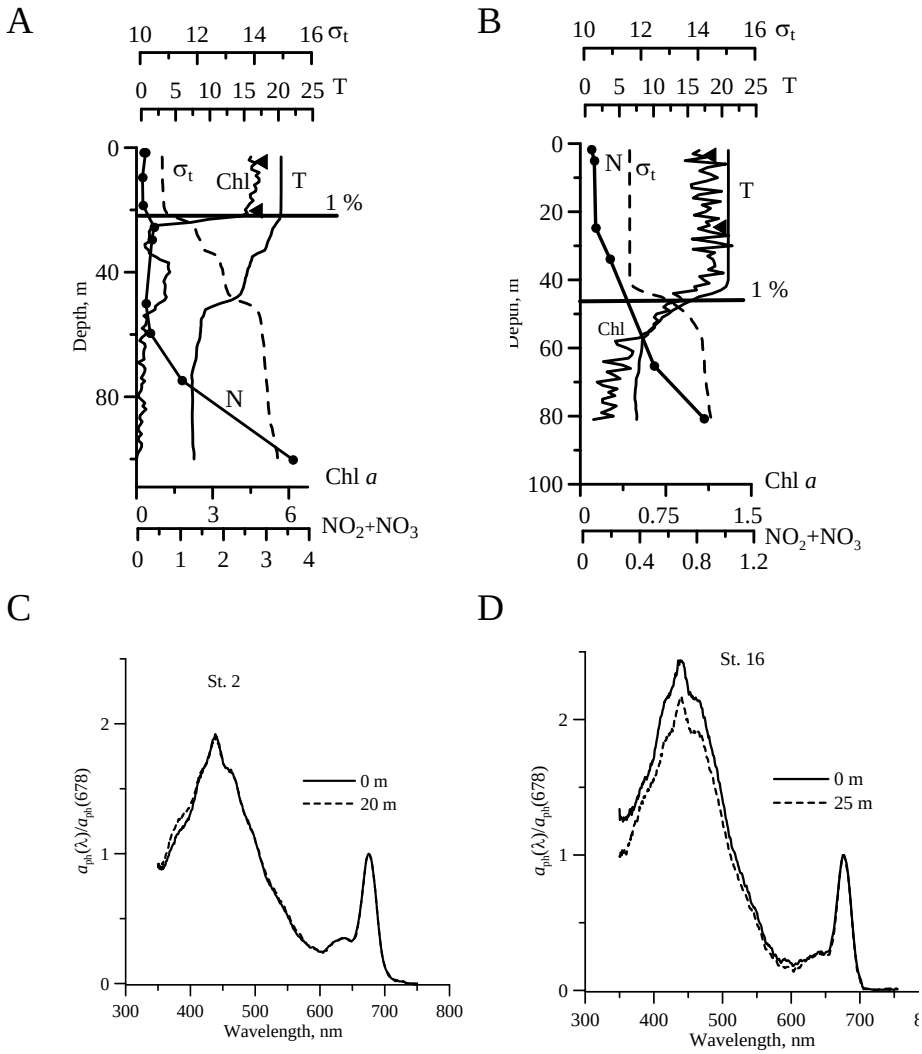

Fig. 3 Typical for the shelf zone vertical profiles of chlorophyll *a* concentration (Chl *a*, mg m^{-3}), temperature (T, ^{0}C), nitrate and nitrite concentration (NO_3+NO_2, μM) and relative density (σ_t, kg m^{-3}) – A, B (Horizontal line shows depth of 1% PAR, ▲– the depths of P-I experiments); Phytoplankton absorption spectra, normalized on coefficient at 678 nm ($a_{ph}(\lambda)/ a_{ph}(678)$) – C, D.

Рис. 3 Типичное для шельфовой зоны вертикальное распределение концентрации хлорофилла *a* (Chl *a*, мг $м^{-3}$), температуры (T, ^{0}C), концентрации нитратов и нитритов (NO_3+NO_2, μM) и относительной плотности ((σ_t, кг $м^{-3}$) (Горизонтальной линией отмечена глубина 1% ФАР, ▲ – глубины экспериментов по определению световых зависимостей фотосинтеза) – A, B; Спектры поглощения света фитопланктоном, нормализованные на величину при 678 нм ($a_{ph}(\lambda)/a_{ph}(678)$) – C, D.

Parameters	Surface (n=13)
Chl *a*	2.6 (±74%)
$a^*_{ph}(678)$	0.0164 (±17%)
R	2.31 (±17%)
$\overline{a}^*_{ph}$	0.0158 (±21%)
ϕ_{max}	0.049 (±68%)

Table 2 Mean values and standard deviation (in a bracket) of some biooptical parameters in the shelf waters.

Табл. 2 Среднее значение и стандартное отклонение (в скобках) биооптических параметров в шельфовых водах

Comments: Chl *a* - chlorophyll *a* concentration, mg m^{-3}; $a^*_{ph}(678)$ - chlorophyll *a* - specific absorption coefficient at red peak, m^2 $(mgChl)^{-1}$; R - blue to red peaks ratio in absorption spectra; $\overline{a}^*_{ph}$ - spectrally averaged chlorophyll a- specific coefficient, m^2 (mg Chl)$^{-1}$ and ϕ_{max} - maxim quantum yield of carbon fixation, mol C (mol quanta)$^{-1}$

Примечание: Chl *a* - концентрация хлорофилла *a,* мг $м^{-3}$; $a^*_{ph}(678)$ - нормированный на хлорофилл *a* коэффициент поглощения света фитопланктоном в красном максимуме, $м^2$ $(мгChl)^{-1}$; R – отношение коэффициентов поглощения в синем и красном максимумах; $\overline{a}^*_{ph}$ - средняя по спектру величина нормированного на хлорофилл *a* коэффициента поглощения света фитопланктоном, $м^2$ $(мгChl)^{-1}$ и ϕ_{max} – максимальный квантовый выход фотосинтеза, мольС (моль квантов)$^{-1}$

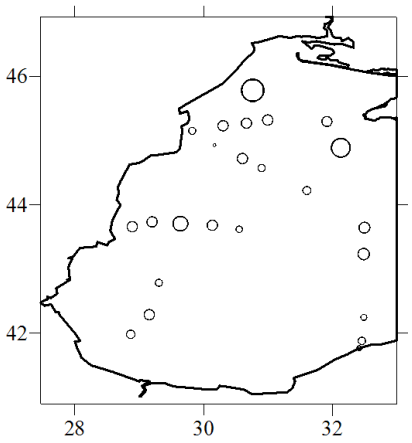

Fig. 4 Spatial distribution of maximum quantum yield of carbon fixation at surface (symbols sizes are proportional to values from 0.009 to 0.107 mol C (mol quanta)$^{-1}$)

Рис. 4 Пространственное распределение максимального квантового выхода фотосинтеза (размер символов - пропорционален значениям от 0.009 до 0.107 Моль С (Моль квантов)$^{-1}$)

For the wide range measured pigment (TChl) concentrations (from 0.3 to 12 mg m^{-3}) the chl*a*-specific absorption coefficients were found to change. For the shelf waters the relationships between a_{ph} in blue ($a_{ph}(438)$) and red ($a_{ph}(678)$) absorption maximum and TChl *a* are described by power function:

$$a_{ph}(438)=0.042\ x^{0.77},\ n=61,\ r^2=0.78 \qquad (7)$$

$$a_{ph}(678)=0.0178\ x^{0.88},\ n=61,\ r^2=0.94 \qquad (8)$$

The increasing of TChl in direction from offshore to shore zone was accompanied with a reduction of chl*a*-specific absorption and smoothing of spectra, which resulted in pronounced decreasing of spectrally averaged chl*a*-specific absorption coefficients. Obtained for shelf waters relationships between $a_{ph}(\lambda)$ and TChl (equations 7 and 8) differ from those for deep-waters region (equations 5 and 6) due to relatively higher range of TChl and more stronger pigment packaging in phytoplankton cells when TChl concentration increased up to 12 mg m^{-3}.

The ϕ_{max} values depended on nutrient availability (Fig. 5).

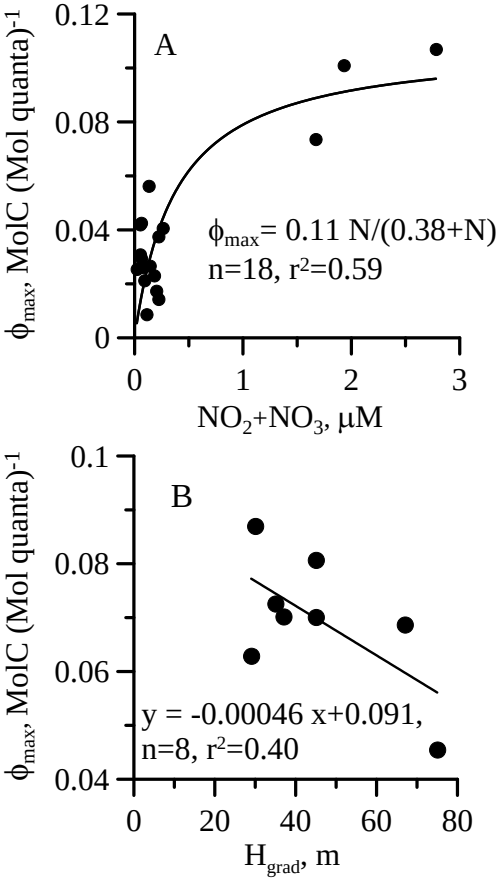

Fig. 5 Relationship between maximum quantum yield of carbon fixation (ϕ_{max}) and nitrate and nitrite concentration (NO_3+NO_2) - A; and distance to maximum gradient of nitrate concentration (H_{grad}) – B.

Рис. 5 Зависимость между максимальным квантовым выходом (ϕ_{max}) и концентрацией нитратов и нитритов (NO_3 +NO_2) – А, и расстоянием до максимального градиента нитратов (H_{grad}) – В.

The surface phytoplankton ϕ_{max} were correlated with nitrate and nitrite concentrations. The relationship between these parameters describes by Michaelis-Menten function with maximum value 0.11 molC (mol quanta)$^{-1}$ and with half-saturation concentration of NO_3 +NO_2 - 0.38 μM. In fact the photochemical assimilation of absorbed quanta was limited by inorganic nitrogen concentration up to 0.76 μM NO_3 +NO_2 and reached its potential maximum under higher NO_3 +NO_2 concentration (>0.76 μM). Analysis of silicate concentration effect on quantum efficiency of photosynthesis showed the positive co-variation between these parameters that apparently, reflects the presence of

diatoms in phytoplankton community, photosynthesis of which requires silicates. Similar character of the dependence of ϕ_{max} on nitrate concentrations was observed for summer phytoplankton in the Black Sea [9], but half saturation constant was lower (0.1μM). In [9] the relationship between ϕ_{max} and nitrate (+nitrite) concentration was analyzed based on data obtained within euphotic layer. Consequently increasing of ϕ_{max} values was related to a rise of nutrient availability and decreasing of light intensity. The effect of light on ϕ_{max} is likely to determine lower value of half saturation constant in comparison with those obtained in our investigation, where the relationship between ϕ_{max} and nutrients was retrieved only for surface samples to minimize the light effect. Our results are in a good agreement with numerous data obtained in the recent laboratory studies, which showed that the relationship between the magnitude of the quantum efficiency of *Dunaliella tertiolecta* and nitrate concentration was described by Michaelis-Menten function [28]. The positive correlation between ϕ_{max} and nutrients concentrations was outlined in Babin et al. [1]. They showed the increasing of ϕ_{max} in the surface layer from oligotrophic to mesotrophic and then to eutrophic site.

Conclusions. Investigations in the western part of the Black Sea during autumn phytoplankton bloom showed high physiological heterogeneity of phytoplankton. Maximum quantum yield of photosynthesis is considered to be the sensitive indicator of physiological status of phytoplankton community related to its nutrient availability. During autumn phytoplankton bloom quantum efficiency of photosynthesis and consequently phytoplankton productivity was limited by nitrate and silicate concentration.

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Поглинання світла і максимальний квантовий вихід фотосинтезу в період осіннього цвітіння фітопланктону в Чорному морі. Т. Я. Чурілова, З. З. Фіненко, С. Тугрул. В межах проекту GEF/UNDP «Black Sea Ecosystem Recovery» проведені визначення впливу забезпеченості біогенними елементами на поглинання світла фітопланктоном і максимальний квантовий вихід фотосинтезу (ϕ_{max}). Концентрація хлорофілу змінювалася від 0.3 до 10 мг м$^{-3}$, зростаючи у напрямку до берега. На мілководних станціях, де верхній перемішаний шар перевищував зону фотосинтезу, був однорідний розподіл хлорофіл *a*. Для профілів хлорофілу *a* в глибоководному районі моря характерний наявність максимуму (DCM) нижче сезонного термоклину. Функціональні характеристики фітопланктону змінювалися з глибиною. Фітопланктон з шару DCM характеризувався на 20% меншими величинами середнього по спектру коефіцієнта поглинання світла (нормованого на хлорофіл *a*) - $\bar{a}^*_{ph}$ (0.016±0.0025 м^2 (мгChl)$^{-1}$) і в ~ 2 рази більшими величинами ϕ_{max} (0.070±0.012 Моль С(Моль квантів)$^{-1}$) порівняно з поверхневими $\bar{a}^*_{ph}$ (0.021±0.0035 м^2 (мгChl)$^{-1}$) і ϕ_{max} (0.030±0.0078 Моль С(Моль квантів)$^{-1}$).

Збільшення поверхневої концентрації хлорофілу *a* в напрямі від глибоководних до прибережних станцій супроводжувалося зменшенням $\overline{a}^{*}_{ph}$ (~20 %) і майже десятиразовим підвищенням ϕ_{max} до теоретично максимальної величини - 0.1 Моль С(Моль квантів)$^{-1}$, що було викликане зростанням концентрації біогенних елементів.

Ключові слова: хлорофіл *a*, фітопланктон, поглинання світла, максимальний квантовий вихід, біогенні елементи

Поглощение света и максимальный квантовый выход фотосинтеза в период осеннего цветения фитопланктона в Чёрном море. Т. Я. Чурилова, З. З. Финенко, С. Тугрул. В рамках проекта GEF/UNDP «Black Sea Ecosystem Recovery» проведены исследования влияния обеспеченности биогенными элементами на поглощение света фитопланктоном и максимальный квантовый выход фотосинтеза (ϕ_{max}). Концентрация хлорофилла изменялась от 0.3 до 10 мг м$^{-3}$, возрастая по направлению к берегу. На мелководных станциях, где верхний перемешанный слой превышал зону фотосинтеза, было однородное распределение хлорофилла *a*. В глубоководном районе моря для профилей хлорофилла *a* было характерно наличие максимума (DCM) ниже сезонного термоклина. Функциональные характеристики фитопланктона изменялись с глубиной. Фитопланктон из слоя DCM характеризовался на 20% меньшими величинами среднего по спектру коэффициента поглощения света (нормированного на хлорофилл *a*) - $\overline{a}^{*}_{ph}$ (0.016±0.0025 м^2 (мгChl)$^{-1}$) и в ~ 2 раза большими величинами ϕ_{max} (0.070±0.012 Моль С(Моль квантов)$^{-1}$) в сравнении с поверхностными $\overline{a}^{*}_{ph}$ (0.021±0.0035 м^2 (мгChl)$^{-1}$) и ϕ_{max} (0.030±0.0078 Моль С(Моль квантов)$^{-1}$). Увеличение концентрации хлорофилла *a* в поверхностном слое в направлении от глубоководных к прибрежным станциям сопровождалось уменьшением $\overline{a}^{*}_{ph}$ (~20 %) и почти десятикратным повышением ϕ_{max} до теоретически максимальной величины - 0.1 Моль С(Моль квантов)$^{-1}$, что было вызвано ростом концентрации биогенных элементов.

Ключевые слова: хлорофилл *a*, фитопланктон, поглощение света, максимальный квантовый выход, биогенные элементы