



Light Absorption by Phytoplankton in the Upper Mixed Layer of the Black Sea: Seasonality and Parametrization

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Specialty section:

This article was submitted to
Ocean Observation,
a section of the journal
Frontiers in Marine Science

Received: 29 December 2016

Accepted: 15 March 2017

Published: 04 April 2017

Citation:

Churilova T, Suslin V, Krivenko O,
Efimova T, Moiseeva N, Mukhanov V
and Smirnova L (2017) Light
Absorption by Phytoplankton in the
Upper Mixed Layer of the Black Sea:
Seasonality and Parametrization.
Front. Mar. Sci. 4:90.
doi: 10.3389/fmars.2017.00090

Standard NASA ocean color algorithm OC4 was developed on the basis of ocean optical data and while appropriate for Case 1 oceanic waters could not be adequately applied for the Black Sea waters due to its different bio-optical properties. OC4 algorithm is shown to overestimate chlorophyll concentration (Chl-*a*) in summer and underestimate Chl-*a* during early spring phytoplankton blooms in the Black Sea. For correct conversion of satellite data to Chl-*a*, primary production and other indicators regional algorithms should be developed taking into account bio-optical properties of the Black Sea waters. Light absorption by phytoplankton pigments— $a_{ph}(\lambda)$ have been measured in open sea and shelf Black Sea waters in different seasons since 1998. It was shown that the first optical depth was located within the upper mixed layer (UML) for most of the year with the exception of the spring when seasonal stratification was developing. As a result spectral features of water leaving radiance were determined by optical properties of the UML. Significant seasonal differences in Chl-*a* specific light absorption coefficients of phytoplankton within UML have been revealed. These differences were caused by adaptive changes of composition and intracellular pigment concentration due to variable environment conditions—mainly light intensity. Empirical relationships between $a_{ph}(\lambda)$ and Chl-*a* were derived by least squares fitting to power functions for different seasons. Incorporation of these results will refine the regional ocean color models and provide improved and seasonally adjusted estimates of chlorophyll *a* concentration, downwelling radiance and primary production in the Black Sea based on satellite data.

Keywords: phytoplankton, light absorption, parameterization, chlorophyll *a* concentration, upper mixed layer, the Black Sea

INTRODUCTION

Visible spectral radiometric data are used widely to assess water productivity (Saba et al., 2011) and to study effect of climate change on ocean productivity (Behrenfeld et al., 2006). Optical scanners of Sea-viewing Wide Field-of-view Sensor (SeaWiFS), MEdium Resolution Imaging Spectrometer (MERIS), Moderate Resolution Imaging Spectroradiometer aboard the Terra and Aqua satellites (MODIS-Aqua/Terra) measure water leaving radiance at several spectral bands (R_{RS}) (Feldman and McClain, 2013). The spectral distribution of R_{RS} is influenced by particulate scattering and absorbance of solar radiance by all in-water optically active components: phytoplankton, non-algal particles (NAP), colored dissolved organic matter (CDOM) and pure water

(Kirk, 1994). Light absorption by particles ($a_p(\lambda)$), phytoplankton ($a_{ph}(\lambda)$), NAP ($a_{NAP}(\lambda)$) and CDOM ($a_{CDOM}(\lambda)$) have been studied in different regions of the global ocean since the 80-s (Hoepffner and Sathyendranath, 1992; Bricaud et al., 1995, 1998; Cleveland, 1995; Babin et al., 2003) to develop algorithms for assessment of water productivity based on remote sensing. Inherent optical properties (IOPs) vary throughout the world ocean. Due to high variability in light absorption and scattering by optically active components, the world ocean needs to be subdivided into various provinces based on regional IOPs, and their features could be used to improve remote-sensing algorithms for each province (Hoepffner and Sathyendranath, 1992; Lutz et al., 1996; Suzuki et al., 1998). Originally the standard NASA algorithm could be applied if there was a high correlation between $a_{ph}(\lambda)$ and absorption by colored dissolved and suspended organic matter ($a_{CDM}(\lambda)$) (Morel and Prieur, 1977). Although NASA standard algorithms are continually being updated (O'Reilly et al., 2000), the latest versions (OC4 for SeaWiFS, and OC3M for MODIS-Aqua/Terra) do not provide an adequate assessment of chlorophyll *a* concentration (Chl-*a*) in the Black Sea waters (Suslin and Churilova, 2016) which belong to the Case 2 (Suslin et al., 2007). Berthon et al. (2008) underlined that important uncertainties for the retrieval of marine products like Chl-*a* still persisted in areas (including the Black Sea) where relatively high CDOM absorption and optically active water constituents CDOM and NAP do not co-vary in a predictable manner with Chl-*a*.

For correct conversion of optical scanner signals into water productivity indices regional algorithms need to be developed taking into account bio-optical properties of the Black Sea. The assessment of the Chl-*a* needs to derive $a_{ph}(\lambda)$ from total light absorption by all optically active components and then estimate Chl-*a* based on relationship between $a_{ph}(\lambda)$ and Chl-*a*. This relationship is also required for development of regional algorithms of downwelling radiance and primary production by spectral approach. Early versions of the regional bio-optical algorithms (Suslin et al., 2008; Churilova et al., 2009; Churilova and Suslin, 2010) were based on limited amount of bio-optical data available. The bio-optical properties of the Black Sea (namely $a_{ph}(\lambda)$, $a_{NAP}(\lambda)$ and $a_{CDOM}(\lambda)$) have been studied since 1995 in open and coastal waters of the Black Sea (Churilova, 2001; Churilova and Berseneva, 2004; Churilova et al., 2004; Chami et al., 2005; Berthon et al., 2008; Dmitriev et al., 2009). Variability in $a_{ph}(\lambda)$ spectral distributions and coefficient values in coastal (Churilova and Berseneva, 2004; Chami et al., 2005; Dmitriev et al., 2009) and open waters (Churilova et al., 2004; Berthon et al., 2008) have been demonstrated but seasonal variability in Chl-*a* specific phytoplankton light absorption coefficients remains not known in details. The bio-optical data measured in the deep waters of the Black Sea from 2011 to 2015 will be examined in this study.

The aim of the current research is to analyze seasonal variability of relationship between phytoplankton light absorption coefficients and chlorophyll *a* concentrations in upper mixed layer (UML) of the Black Sea and derive season-specific modeling parameters.

MATERIALS AND METHODS

Sampling

Bio-optical measurements were carried out during 7 cruises of RV "Professor Vodyanitsky" in different seasons during 2011–2015 in the deep-water areas (deeper 100 m isobath) of Black Sea (Table 1, Figure 1). Water samples were collected at 5–7 depths within euphotic zone with 10 liter Niskin bottles of CTD/rosette system MARK-III (Neil Brown Ocean Sensors, Inc) or SBE-911plus (Sea Bird Electronics). Sampling depths were chosen based on water transparency by Secchi disc depth (Z_s), as well as temperature and salinity profiles measured by CTD system. The euphotic zone (Z_{eu}), determined as penetration depth for 1% of photosynthetically available radiance (PAR), was calculated based on the light (I) attenuation with depth (z) (Kirk, 1994):

$$I(z) = I(0) \times e^{(-K_d \times z)}, \quad (1)$$

where K_d —light attenuation coefficient on average for both euphotic layer and for visible light waves (400–700 nm). Z_{eu} was calculated based on the Equation (1):

$$Z_{eu} = \frac{4.6}{K_d} \quad (2)$$

Values of K_d were estimated based on the relationship between K_d and Z_s obtained for the Black Sea (Vedernikov, 1989). Average light intensity in the UML (PAR_{UML}) was estimated in accordance with (Babin et al., 1996):

$$PAR_{UML} = PAR(0) \times \frac{\left(1 - e^{(-4.6 \times \frac{Z_{uml}}{Z_{eu}})}\right)}{\left(4.6 \times \frac{Z_{uml}}{Z_{eu}}\right)}, \quad (3)$$

where $PAR(0)$ —PAR at the sea surface, data from Suslin et al. (2015), Z_{uml} —UML depth was determined using temperature difference criterion (0.5°C) and mean water temperature at 0–3 m as reference level. Optical depth (ζ) of Z_{uml} was assessed using K_d calculated based on Z_s (Vedernikov, 1989).

Pigment Analysis

For chlorophyll and phaeopigment concentration analysis 1–2 L water samples were gently vacuum filtered (<25 kPa)

TABLE 1 | Information about scientific cruises of RV Professor Vodyanitsky (PV) in the Black Sea.

| Cruise | Year | Date | Investigation area of the Black Sea |
|--------|------|------------------------|-------------------------------------|
| PV 69 | 2011 | 2–11 August | Deep western |
| PV 70 | 2011 | 19–27 August | Deep western |
| PV 77 | 2014 | 3–7 September | Deep eastern |
| PV 78 | 2014 | 28 November–9 December | Deep eastern |
| PV 79 | 2015 | 25–30 September | Deep eastern |
| PV 81 | 2015 | 3–10 November | Deep western |
| PV 82 | 2015 | 5–9 December | Deep eastern |

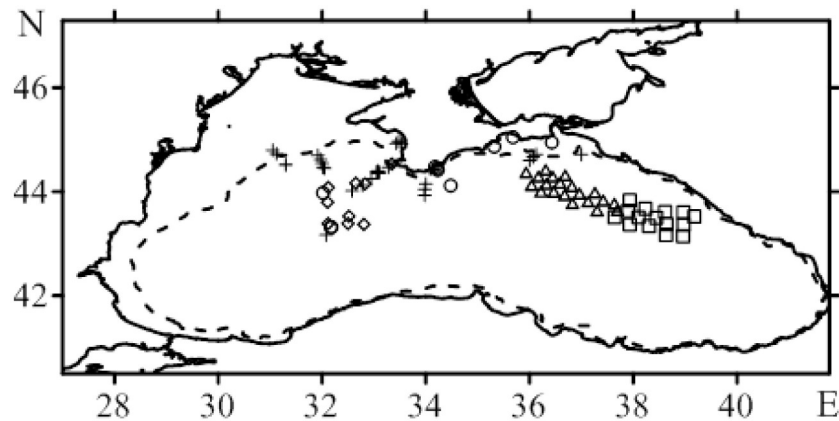


FIGURE 1 | Map of bio-optical stations in the scientific cruises on RV Professor Vodyanitskiy (PV) in the Black Sea: \times 69 (crosses), 70 (circles), 77 (square), 78 (square, triangles), 79 (triangles), 81 (rhombs), 82 (triangles). The dotted line defines the 100 m isobath.

onto 25 mm diameter Whatman GF/F glass fiber filters. Filters were wrapped in an aluminum foil and stored in a liquid nitrogen until analysis on a laboratory. Filters were placed in 5 ml of 90% acetone in a 10 ml glass centrifuge tube, then were treated with vibration for 20 s using a vibration mixer (FALK Falc instruments, Italy), extracted at 5°C or below, for at least 10 h and then centrifuged. The above procedure was repeated using an additional 5 ml of 90% acetone for a more complete extraction of phytoplankton pigments. The second extraction of the pigments contributed 15% on average to total concentration values. The extracts were then analyzed for pigment content by spectrophotometric method (Lorenzen, 1967; Jeffrey and Humphrey, 1975) using spectrophotometer Lambda 35 (Perkin Elmer). Proportion of non-photosynthetic pigments in the total phytoplankton pigment content (NPP) was determined in accordance with relationship between environmental light condition (PAR) and NPP proposed by Babin et al. (1996).

Phytoplankton Light Absorption

Optical densities of particulate matter were determined by the filter pad technique (“wet filter technique”) (Yentsch, 1962; Mitchell and Kiefer, 1988). $a_{ph}(\lambda)$ was determined by the difference between $a_p(\lambda)$ and $a_{NAP}(\lambda)$:

$$a_{ph}(\lambda) = a_p(\lambda) - a_{NAP}(\lambda) \quad (4)$$

Values of $a_{ph}(\lambda)$ were obtained from optical densities after correction for differential scattering (setting the mean absorption between 740 and 750 nm to zero) and for the path length amplification factor, converting decimal to natural logarithms, taking into account the volume filtered and the filter area of filtration, and subtracting $a_{NAP}(\lambda)$ (Churilova, 2001). The sample optical densities were measured from 350 to 750 nm on Perkin Elmer Lambda 35 spectrophotometer equipped with an integrating sphere. $a_{NAP}(\lambda)$ values were experimentally determined using the chemical (bleaching by NaClO solution) method (Tassan and Ferrari, 1995).

The path length amplification factor (beta-correction) was estimated applying the quadratic equation described by Mitchell (1990). To get Chl-*a* specific light absorption coefficients of phytoplankton ($a_{ph}^*(\lambda)$) the values of $a_{ph}(\lambda)$ (m^{-1}) were divided by the sum of chlorophyll *a* and phaeopigments concentrations (Chl-*a*) ($mg\ m^{-3}$). Relationships between $a_{ph}(\lambda)$ and Chl-*a* were derived by least squares fitting to power functions for visible spectral domain 400–700 nm with 1 nm resolution.

Phytoplankton

Identification of phytoplankton species (micro- and nano-size fractions), counting of cells and cell size measurements were performed with transmission microscope Ergaval (Carl Zeiss Jena) using Naumann chamber. Water samples (2–5 L) were concentrated by inverse filtration method using nuclepore filters with 1 μm pore diameter. The concentrated samples were fixed with a solution (4% final concentration) of 25 g paraformaldehyde dissolved in 100 ml of hot (80°C) 25% glutaraldehyde, clarified with few drops of 1 N NaOH solution. Cells were sized and its volumes were assessed using geometrical figures (sphere, ellipsoid or cylinder) corresponding to the cell shapes. Phytoplankton analysis was conducted only at selected stations in August 2011, September 2014 and December 2014, 2015.

In August 2011, September 2014 and December 2014, 2015 flow cytometric analysis was performed by flow cytometer Cytomics FC 500 (Beckman Coulter, USA) equipped with a single-phase argon laser (488 nm) (Marie et al., 1999; Schapira et al., 2010). For all detected particles phycoerythrin fluorescence emission (575 nm), and chlorophyll fluorescence emission (675 nm) were measured. The samples were fixed with formaldehyde (final concentration 2%) immediately after the sampling, then the samples were frozen in liquid nitrogen (−80°C) and stored at −20°C until analysis in the laboratory. The cytometer measurements were calibrated by the addition of a known concentration of the Fluorospheres Flow-CheckTM (Beckman

Coulter). Cytometric data were analyzed using CXP software (Beckman Coulter).

RESULTS

Chlorophyll *a* Concentration

Chl-*a* in surface layer of the deep water regions of the Black Sea were low in a summer. In the deep western part of the sea in August 2011 (Figure 1) Chl-*a* in the UML were in a range 0.15–0.30 mg·m⁻³. At this time, seasonal thermocline was well developed with maximum of temperature gradient 3.3 ± 1.1°C m⁻¹ at the 12 ± 2.3 m depth, where optical depth (ζ) was 1.5 ± 0.42 (Table 2). In August water transparency was high. Values of Z_s and K_d were 16 ± 2.1 m and 0.12 ± 0.013 m⁻¹, correspondingly. Z_{eu} values were 37 ± 4.0 m. Vertical Chl-*a* profiles were characterized by rather homogeneous Chl-*a* distribution within UML and deep Chl-*a* maximum (DCM) located near the bottom of the euphotic zone with Chl-*a* values 5–10 times higher than in the UML (Figure 2). In the surface layer of the deep eastern part of the Black Sea in September 2014 and 2015 (Figure 1) Chl-*a* values (0.21–0.35 mg·m⁻³) were very similar to these measured in summer. In September maximum temperature gradient (4.3 ± 1.2°C m⁻¹) and its location (9.5 ± 2.7 m with $\zeta = 1.1 \pm 0.40$) were similar to those observed in the summer. Vertical Chl-*a* distribution was similar to that observed in August (Figure 2), but with less variability in Chl-*a*: Chl-*a* concentration in the DCM was 3 times higher than in the UML in comparison with 5–10 times differences in August. Water transparency in the August and September was comparable ($Z_s = 16 \pm 1.4$ m; $K_d = 0.12 \pm 0.0073$ m⁻¹; $Z_{eu} = 38 \pm 2.6$ m).

In the western deep part of the Black Sea in the late autumn (November 2015) the seasonal thermocline was substantially destructed. It resulted in an enlargement of the UML (28 ± 3.4 m), which become ~3 times deeper than in the summer (Figure 2). Chl-*a* in the surface layer in November 2015 varied from 0.54 to 1.4 mg m⁻³ with less transparency ($Z_s = 13 \pm 1.0$ m; $K_d = 0.15 \pm 0.009$ m⁻¹) (Table 2). Maximum temperature gradient (1.5 ± 0.38°C m⁻¹) was located at the optical depth of 4.2 ± 0.72. Consequently, Z_{eu} (31 ± 2.0 m) was close to UML depth. Chl-*a* was distributed homogeneously within UML and decreased sharply in thermocline (Figure 2). Thus, vertical pigment distribution in November contrasted with that in summer, when seasonal thermocline divided euphotic zone into two quasi isolated layers with different environments. In fact, in late autumn phytoplankton was present in UML only. In December 2014 and 2015 in surface layer of eastern deep water part of the Black Sea (Figure 1) Chl-*a* varied from 1.0 to 2.0 mg m⁻³ (1.3 ± 0.25 mg m⁻³). UML was 32 ± 7.0 m. Vertical distribution of Chl-*a* was homogeneous within UML similar to Chl-*a* profiles observed in western waters in November 2015. In December Z_s and K_d were equal to November 2015 data (12 ± 2.5 m and 0.15 ± 0.023 m⁻¹, correspondingly). Maximum temperature gradient was 0.93 ± 0.45°C m⁻¹ and located at optical depths of 4.9 ± 1.2 (Table 2). Consequently, in December euphotic zone (30 ± 4.9 m) occurred within UML as it was observed in November. In both December and November phytoplankton was present within UML only.

Phytoplankton

In August 2011 in UML of western deep waters of the Black Sea phytoplankton was dominated by dinoflagellates. Wet biomass of phytoplankton was 540 ± 310 mg·m⁻³ on average. Assuming intracellular organic carbon (C) content at 10% of wet biomass, C to Chl-*a* ratio (C/Chl-*a*) was 145 ± 76 mg mg⁻¹. Biomass of photosynthetic picoplankton was 2.7 ± 0.46 mg·m⁻³ on average. The contribution of picoplankton to total phytoplankton biomass was <1%. In September 2014 phytoplankton biomass in UML was assessed at selected stations. Wet biomass was ~450 mg m⁻³. The phytoplankton was dominated mainly (50–70%) by dinoflagellates *Gymnodinium* spp (*Gymnodinium fungiforme* and *Gymnodinium paululum*). C/Chl-*a* ratio was ~110 mg mg⁻¹. Photosynthetic picoplankton biomass was equal 1.7 ± 1.0 mg·m⁻³ on average and its contribution to total phytoplankton biomass was < 1%. In December 2014 and 2015 wet phytoplankton biomass in UML varied from 190 to 430 mg m⁻³. In 2014 *Proboscia alata* dominated (by biomass) in phytoplankton community. In 2015 phytoplankton was represented mainly by large diatoms *Pseudosolenia calcar-avis* with cell volume 19000–83000 μ m³. C/Chl-*a* ratio was ~25–40 mg mg⁻¹. In December 2014 and 2015 biomass of photosynthetic picoplankton was 11.0 ± 4.9 and 13.0 ± 4.4 mg·m⁻³ on average correspondingly, and picoplankton contribution to total phytoplankton biomass was ~5%.

Phytoplankton Light Absorption

Phytoplankton light absorption spectra measured in UML are presented on Figure 3. To examine the relationship between $a_{ph}(\lambda)$ and Chl-*a* in the UML results were grouped into 2 datasets: (1) summer dataset that included results from August 2011, September 2014, 2015; (2) winter dataset with results from November 2014, December 2014 and 2015 (Table 1). September 2014, 2015 was considered part to the summer season, due to persistence of strong seasonal stratification with typical “summer” type of vertical distribution of pigments. November 2015 was considered part of winter, because of water column structure similarity to that in December 2014 and 2015. In November depths of UML and euphotic zone were close and all phytoplankton was present within UML as it was in December.

In the $a_{ph}(\lambda)$ spectra two main peaks were observed: in blue (near 440 nm) and red (near 678 nm) spectrum domains (Figure 3). The seasonal differences in the phytoplankton light absorption were manifested in both spectral shapes and values of chlorophyll *a* specific coefficients. In the summer $a_{ph}^*(\lambda)$ were relatively high in the blue spectrum domain. Ratio between blue and red peaks (R) was 3.4 (± 0.61) on average in summer, which was significantly higher than in winter (2.2 ± 0.45) (Figure 3). In both winter and summer R values decreased if Chl-*a* increased. The variations of $a_{ph}(\lambda)$ as a function of Chl-*a* are shown in Figure 4 at two wavelengths (~440 and 678 nm) corresponding to the blue and red peaks of the spectra. To describe the relationship between $a_{ph}(\lambda)$ and Chl-*a* a power function was used (Figure 4):

$$a_{ph}(\lambda) = A(\lambda) \times (\text{Chl-}a)^{B(\lambda)}, \quad (5)$$

TABLE 2 | Hydrophysical characteristics: maximum temperature gradient (ΔT) and depth (Z_{tc})/optical depth (ζ) of its location; Secchi disc depth visibility (Z_s); euphotic zone (Z_{eu}); diffuse attenuation coefficient for downwelling irradiance over the Z_{eu} (K_d); photosynthetically available radiance incident on the Black Sea surface [PAR(0)] and averaged over upper mixed layer [PAR(UML)].

| | Z_{tc} , m | ζ | ΔT , °C m ⁻¹ | PAR (UML), E m ⁻² d ⁻¹ | Z_s , m | K_d , m ⁻¹ | Z_{eu} , m | PAR(0), E m ⁻² d ⁻¹ |
|-------------------------------|--------------|---------|---------------------------------|--|-----------|-------------------------|--------------|---|
| AUGUST (2011) | | | | | | | | |
| mean | 12 | 1.5 | 3.3 | 27 | 16 | 0.12 | 37 | 52 |
| SD | 2.3 | 0.42 | 1.1 | 8.1 | 2.1 | 0.013 | 4.0 | 1.2 |
| min | 8.0 | 0.84 | 2.2 | 31 | 12 | 0.10 | 30 | 46 |
| max | 13 | 2.0 | 5.7 | 24 | 20 | 0.15 | 46 | 56 |
| SEPTEMBER (2014, 2015) | | | | | | | | |
| mean | 9.5 | 1.1 | 4.3 | 22.5 | 16 | 0.12 | 38 | 38 |
| SD | 2.7 | 0.40 | 1.2 | 2.9 | 1.4 | 0.0073 | 2.6 | 4.1 |
| min | 5 | 0.55 | 2.9 | 21 | 12 | 0.11 | 30 | 28 |
| max | 14 | 2.1 | 7.8 | 31 | 17 | 0.15 | 45 | 46 |
| NOVEMBER (2015) | | | | | | | | |
| mean | 28 | 4.2 | 1.5 | 3.9 | 13 | 0.15 | 31 | 17 |
| SD | 3.4 | 0.72 | 0.38 | 1.2 | 1.0 | 0.0090 | 2.0 | 2.5 |
| min | 24 | 3.12 | 1.0 | 2.0 | 11 | 0.13 | 28 | 9 |
| max | 35 | 5.6 | 2.1 | 8.6 | 14 | 0.16 | 34 | 22 |
| DECEMBER (2014, 2015) | | | | | | | | |
| mean | 32 | 4.9 | 0.93 | 2.4 | 12 | 0.15 | 30 | 12 |
| SD | 7.0 | 1.2 | 0.45 | 0.8 | 2.5 | 0.023 | 4.9 | 1.7 |
| min | 27 | 2.9 | 0.24 | 2.5 | 7 | 0.11 | 20 | 7.8 |
| max | 55 | 12.7 | 2.0 | 1.2 | 19 | 0.23 | 43 | 15 |

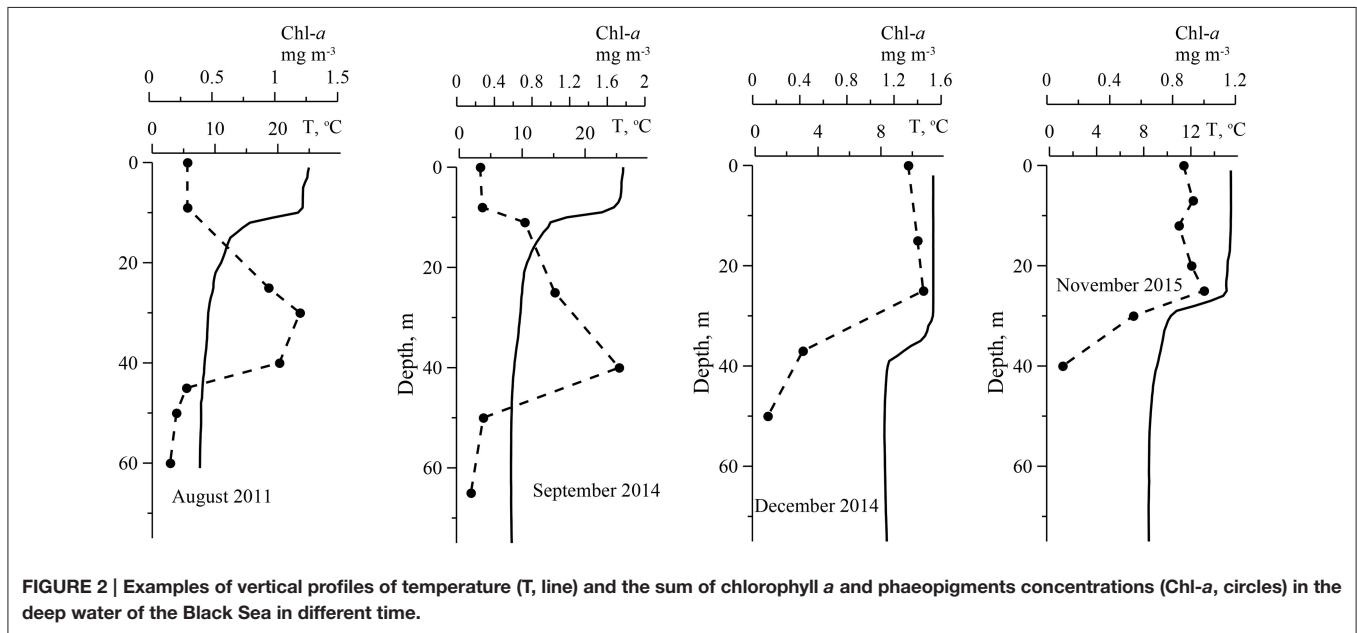


FIGURE 2 | Examples of vertical profiles of temperature (T, line) and the sum of chlorophyll a and phaeopigments concentrations (Chl-a, circles) in the deep water of the Black Sea in different time.

where $A(\lambda)$ —spectral coefficient, which is equal to $a_{ph}^*(\lambda)$ in case when Chl-a equal to 1 mg m^{-3} .

For two data sets following fit equations were obtained (Figure 4):

(1) In summer:

$$a_{ph}(440) = 0.076 \times (\text{Chl-a})^{0.84} (r^2 = 0.66) \quad (6)$$

$$a_{ph}(678) = 0.024 \times (\text{Chl-a})^{0.95} (r^2 = 0.63) \quad (7)$$

(2) In winter:

$$a_{ph}(440) = 0.045 \times (\text{Chl-a})^{0.81} (r^2 = 0.78) \quad (8)$$

$$a_{ph}(678) = 0.021 \times (\text{Chl-a})^{0.95} (r^2 = 0.88) \quad (9)$$

To infer $a_{ph}(\lambda)$ spectral distribution from Chl-a relationship between these parameters needs to be determined for entire visible spectrum (400–700 nm). Based on two empirical data sets the $a_{ph}(\lambda)$ vs Chl-a dependencies were parameterized

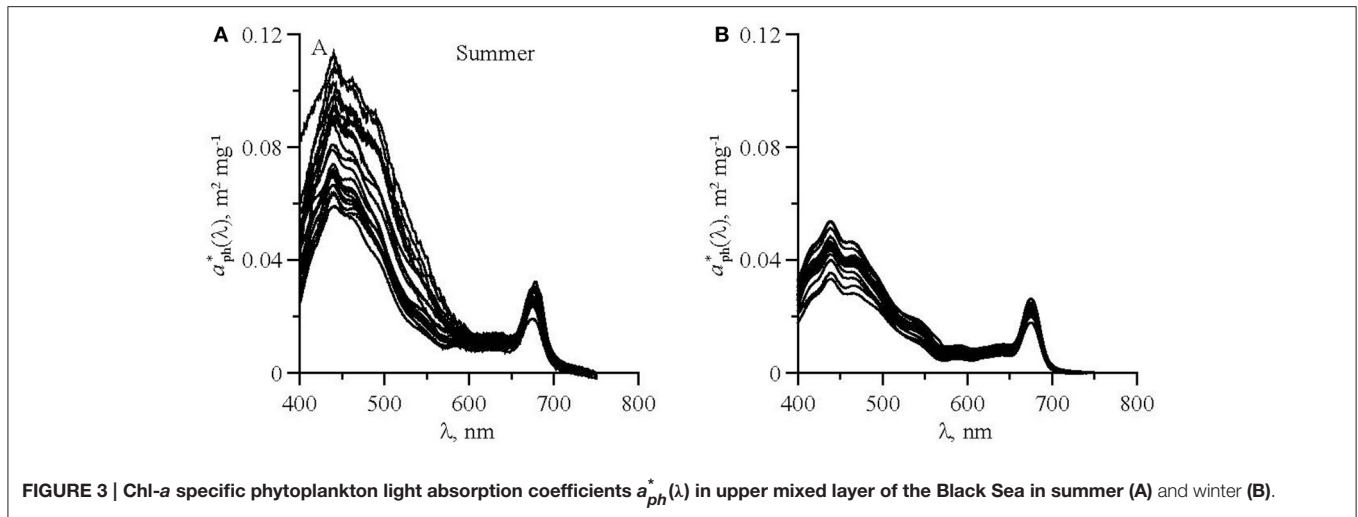


FIGURE 3 | Chl-*a* specific phytoplankton light absorption coefficients $a_{ph}^*(\lambda)$ in upper mixed layer of the Black Sea in summer (A) and winter (B).

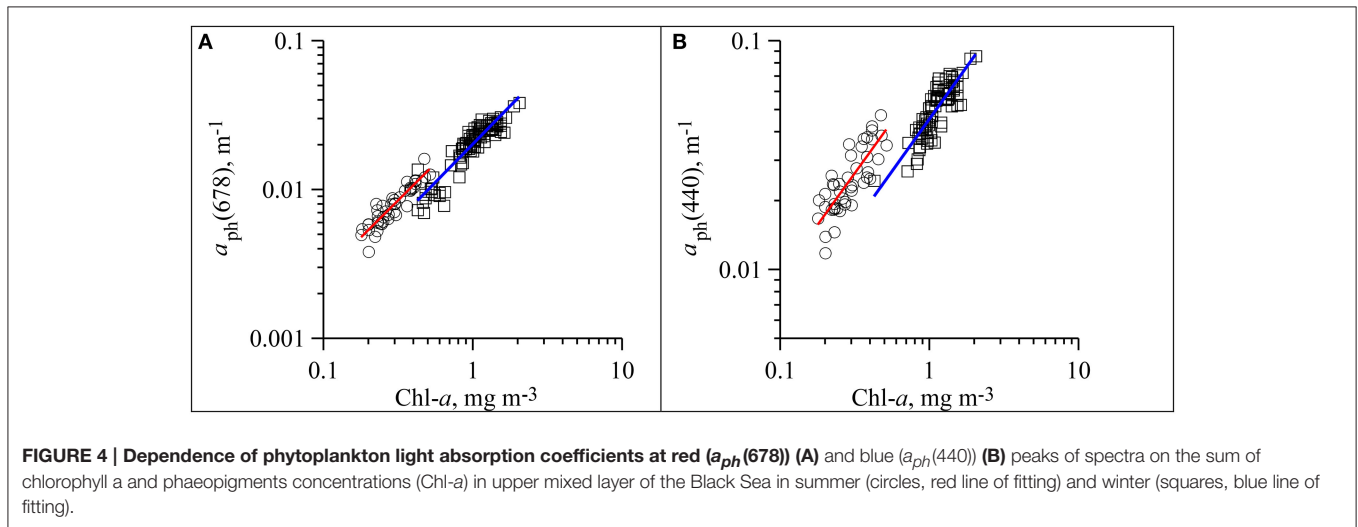


FIGURE 4 | Dependence of phytoplankton light absorption coefficients at red ($a_{ph}(678)$) (A) and blue ($a_{ph}(440)$) (B) peaks of spectra on the sum of chlorophyll *a* and phaeopigments concentrations (Chl-*a*) in upper mixed layer of the Black Sea in summer (circles, red line of fitting) and winter (squares, blue line of fitting).

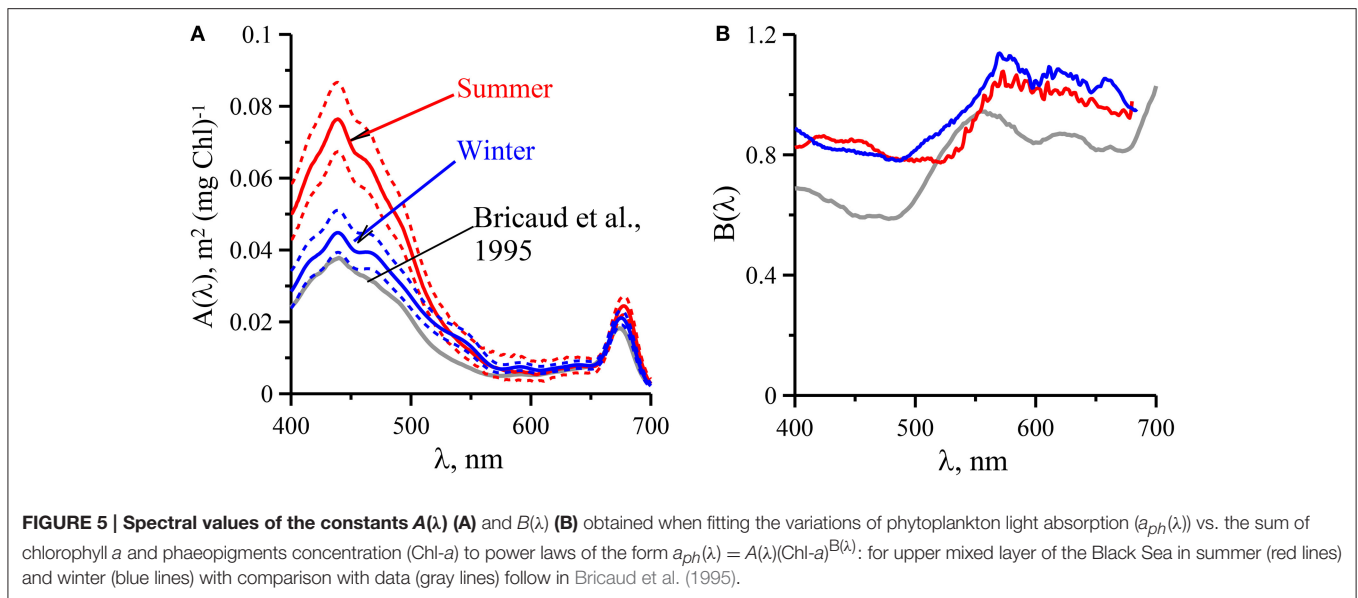
using Equation (5) for summer and winter. The results of the parameterization performed from 400 to 700 nm with 1 nm spectral resolution are presented in **Figure 5** and in **Tables 3, 4**. It is evident that $a_{ph}^*(\lambda)$ values are higher in summer than those in winter (**Figure 3**). This seasonal difference is more pronounced in the blue spectrum domain. For summer phytoplankton the value of $A(\lambda)$ coefficient at 440 nm is about twice higher than that for winter.

Photosynthetically available radiance incident on the Black Sea surface [PAR(0)] varied seasonally (Suslin et al., 2015). In August and September PAR(0) was on average 52 ± 1.2 and $38 \pm 2.6 \text{ E m}^{-2} \text{ d}^{-1}$ correspondingly (**Table 2**). In November and December PAR(0) was 17 ± 2.5 and $12 \pm 1.7 \text{ E m}^{-2} \text{ d}^{-1}$, which were about 3 times lower than those in warm months. PAR in UML depends not only on PAR(0) but also on water transparency and ratio between Z_{UML} and Z_{eu} . In winter, waters were less transparent than in summer. Moreover, UML was comparable with Z_{eu} in winter while in summer Z_{UML} was located between first and second optical depths. As results PAR in UML differed

more (~ 10 times) between summer and winter in comparison with seasonal dynamics of PAR(0) (**Table 2**). PAR in UML was equal in August and September 27 ± 8.1 and $23 \pm 2.9 \text{ E m}^{-2} \text{ d}^{-1}$, correspondingly (**Table 2**). In November and December PAR in UML was equal 3.9 ± 1.2 and $2.4 \pm 0.8 \text{ E m}^{-2} \text{ d}^{-1}$, correspondingly (**Table 2**).

DISCUSSION

The first optical depth which determines water leaving radiance spectral patterns (Gordon and McGlunev, 1975) detectable by remote scanners is located within the UML in the deep open waters of the Black Sea. It should be noted that K_d averaged over the euphotic zone was used in our assessment. However, domination of CDOM in total light absorption in the Black Sea results in sharply decreasing K_d values with depth. In the subsurface layer K_d values were estimated to be ~ 1.6 times higher than mean K_d for euphotic zone (Churilova et al., 2009). Therefore, in our assessment Z_{uml} was



underestimated by using average K_d . In fact, it gives more reasonable conclusion about location of the first optical depth within UML. Consequently, bio-optical properties of the UML in the Black Sea determine remotely sensed optical signals and could be used for development and refining of the regional models of productivity indicators.

Analysis of the link between phytoplankton light absorption coefficients and chlorophyll *a* concentration revealed seasonal differences in UML (Figures 3, 4 and Tables 3, 4) which were related to difference of $a_{ph}^*(\lambda)$ values between summer and winter. The difference was more pronounced in the blue spectrum domain (Figure 3). In summer values of parameterization coefficient $A(\lambda)$ relevant to red and blue peaks were on average 15 and 70% higher than those for winter (Figure 5), respectively. Seasonal differences in normalized (on Chl-*a*) phytoplankton light absorbance capacity were related to strong changes in environmental conditions in UML, mainly due to the averaged PAR within UML (Figure 6). Observed seasonal dynamics of (UML) and euphotic zone in the deep open waters of the Black Sea are consistent with intraannual changes of these parameters (Z_{uml} and Z_{eu}) in the Black Sea outlined earlier (Ivanov and Belokopytov, 2011; Agirbas et al., 2014).

In winter [PAR(0)] decreased but the ratio between Z_{UML} and Z_{eu} increased in comparison with summer. As the result in winter average light field within UML decreased in almost 10-fold in comparison with PAR_{UML} in summer. Seasonal changes of environmental conditions in UML caused ~ 5 – 7 fold variability in C/Chl-*a* ratio between winter and summer. Observed C/Chl-*a* variability agrees with a change of intracellular concentration of chlorophyll *a* (MacIntyre et al., 2002; Behrenfeld et al., 2005) due to physiological acclimation of algae cultures and phytoplankton to light intensity decreased in the same range as PAR varied in the UML of the Black Sea. Intracellular pigment concentration defines degree of pigment packaging, which in turn effects on

$a_{ph}^*(\lambda)$ (Morel and Bricaud, 1981; Bidigare et al., 1990; Hoepffner and Sathyendranath, 1991; Kirk, 1994; Fujiki and Taguchi, 2002). In the current research it was shown that $a_{ph}^*(\lambda)$ and C/Chl-*a* were significantly less in winter than values of those parameters in summer, which were relevant to “pigment packaging” effected on $a_{ph}^*(\lambda)$ at red peak (~ 678 nm) where light quanta are absorbed by chlorophyll *a* and phaeopigments only (Jeffrey et al., 1997). At shorter wavelengths (in blue spectrum domain) seasonal variation in $a_{ph}^*(\lambda)$ was more pronounced than at red wavelengths (Figure 3). In the blue part of the spectrum besides chlorophyll *a*, other accessory pigments absorb light quanta (Bidigare et al., 1990; Jeffrey et al., 1997) which lead to “smoothing” of spectra due to accessory pigment “packaging” if Chl-*a* specific absorption coefficients are considered. Ratio of accessory pigment-to-Chl-*a* changes due to photoacclimation of algae (MacIntyre et al., 2002; Grant and Louda, 2010), which is related mainly to photoprotective (i.e., non-photosynthetic) pigments (NPP). In review of photoacclimation of different microalgae taxons it was shown that \sim order increase of light intensity resulted in ~ 3 – 4 times increase of photoprotective xanthophyll to Chl-*a* ratio on average (Figure 9 in MacIntyre et al., 2002). Investigations of phytoplankton accessory pigments variability have demonstrated that photoprotective pigments tend to be greater in the surface low Chl-*a* waters at latitudes where radiance incident on the sea surface is relatively high (Stuart et al., 1998; Barlow et al., 2004; Sathyendranath et al., 2005). Variability of $R(a_{ph}(440)/a_{ph}(678))$ was shown to be correlated with NPP to Chl-*a* ratio (Lutz et al., 2003). Altogether the increase of $a_{ph}^*(440)$ is related to low Chl-*a* waters with lower intracellular concentrations of pigments, and a greater proportion of photoprotective pigments occurred in stratified, high light, nutrient-limited regions (Bricaud et al., 1995; Cleveland, 1995; Aguirre-Hernandez et al., 2004). In general these results are in a good agreement with the Black Sea observations. Although in current research pigment composition

TABLE 3 | Spectral values of the constant obtained when fitting the variations of $a_{ph}(\lambda)$ vs. the (chlorophyll *a* + phaeopigment) concentration (Chl-*a*) to power laws of the form.

| λ | A(λ) | SD | B(λ) | λ | A | SD | B(λ) |
|-----------|----------------|---------|----------------|-----------|-------|---------|----------------|
| 400 | 0.050 | 0.00779 | 0.82 | 544 | 0.013 | 0.00332 | 0.88 |
| 402 | 0.051 | 0.00774 | 0.83 | 546 | 0.013 | 0.00333 | 0.88 |
| 404 | 0.052 | 0.00777 | 0.83 | 548 | 0.012 | 0.00329 | 0.91 |
| 406 | 0.054 | 0.00799 | 0.83 | 550 | 0.012 | 0.00315 | 0.92 |
| 408 | 0.056 | 0.00805 | 0.83 | 552 | 0.011 | 0.00319 | 0.94 |
| 410 | 0.058 | 0.00813 | 0.84 | 554 | 0.010 | 0.00319 | 0.95 |
| 412 | 0.060 | 0.00845 | 0.84 | 556 | 0.010 | 0.00296 | 0.97 |
| 414 | 0.061 | 0.0086 | 0.85 | 558 | 0.009 | 0.00302 | 1.00 |
| 416 | 0.063 | 0.0087 | 0.86 | 560 | 0.009 | 0.00323 | 0.98 |
| 418 | 0.064 | 0.00896 | 0.86 | 562 | 0.008 | 0.00363 | 0.99 |
| 420 | 0.065 | 0.00901 | 0.86 | 564 | 0.008 | 0.00323 | 1.03 |
| 422 | 0.066 | 0.00911 | 0.86 | 566 | 0.008 | 0.00311 | 1.04 |
| 424 | 0.067 | 0.00949 | 0.86 | 568 | 0.007 | 0.00358 | 1.03 |
| 426 | 0.069 | 0.00966 | 0.86 | 570 | 0.007 | 0.00343 | 1.04 |
| 428 | 0.070 | 0.00974 | 0.86 | 572 | 0.007 | 0.00334 | 1.07 |
| 430 | 0.071 | 0.00989 | 0.85 | 574 | 0.007 | 0.00319 | 1.06 |
| 432 | 0.073 | 0.00991 | 0.85 | 576 | 0.007 | 0.00331 | 1.03 |
| 434 | 0.075 | 0.00983 | 0.84 | 578 | 0.006 | 0.00354 | 1.03 |
| 436 | 0.076 | 0.00977 | 0.84 | 580 | 0.006 | 0.00316 | 1.03 |
| 438 | 0.076 | 0.0097 | 0.85 | 582 | 0.006 | 0.00333 | 1.05 |
| 440 | 0.076 | 0.00946 | 0.84 | 584 | 0.006 | 0.00325 | 1.06 |
| 442 | 0.076 | 0.00941 | 0.85 | 586 | 0.006 | 0.00375 | 1.03 |
| 444 | 0.074 | 0.00934 | 0.84 | 588 | 0.006 | 0.00319 | 1.01 |
| 446 | 0.072 | 0.00914 | 0.85 | 590 | 0.006 | 0.00308 | 1.04 |
| 448 | 0.071 | 0.00898 | 0.85 | 592 | 0.006 | 0.00335 | 1.05 |
| 450 | 0.069 | 0.00876 | 0.84 | 594 | 0.006 | 0.00323 | 1.05 |
| 452 | 0.068 | 0.00888 | 0.85 | 596 | 0.006 | 0.00307 | 1.01 |
| 454 | 0.067 | 0.00873 | 0.85 | 598 | 0.006 | 0.0029 | 1.01 |
| 456 | 0.066 | 0.00871 | 0.85 | 600 | 0.006 | 0.00274 | 1.02 |
| 458 | 0.066 | 0.00875 | 0.84 | 602 | 0.006 | 0.00291 | 1.02 |
| 460 | 0.065 | 0.00865 | 0.84 | 604 | 0.005 | 0.00286 | 1.02 |
| 462 | 0.065 | 0.00856 | 0.83 | 606 | 0.005 | 0.00258 | 0.99 |
| 464 | 0.064 | 0.00842 | 0.83 | 608 | 0.006 | 0 | 1.01 |
| 466 | 0.063 | 0.00849 | 0.82 | 610 | 0.006 | 0.00289 | 1.04 |
| 468 | 0.062 | 0.00846 | 0.82 | 612 | 0.006 | 0.00281 | 1.00 |
| 470 | 0.061 | 0.00804 | 0.81 | 614 | 0.006 | 0.00261 | 1.01 |
| 472 | 0.059 | 0.00796 | 0.81 | 616 | 0.006 | 0.00257 | 1.02 |
| 474 | 0.058 | 0.00779 | 0.80 | 618 | 0.006 | 0.00237 | 1.01 |
| 476 | 0.056 | 0.00765 | 0.79 | 620 | 0.007 | 0.00246 | 1.00 |
| 478 | 0.055 | 0.00759 | 0.79 | 622 | 0.007 | 0.00253 | 1.00 |
| 480 | 0.054 | 0.00738 | 0.79 | 624 | 0.007 | 0.00251 | 1.02 |
| 482 | 0.053 | 0.00731 | 0.79 | 626 | 0.007 | 0.00217 | 1.02 |
| 484 | 0.051 | 0.00719 | 0.79 | 628 | 0.007 | 0.00223 | 1.01 |
| 486 | 0.051 | 0.00708 | 0.78 | 630 | 0.007 | 0.00248 | 1.00 |
| 488 | 0.049 | 0.00692 | 0.79 | 632 | 0.007 | 0.00227 | 1.01 |
| 490 | 0.048 | 0.00684 | 0.78 | 634 | 0.007 | 0.00212 | 0.99 |
| 492 | 0.047 | 0.00664 | 0.79 | 636 | 0.008 | 0.00214 | 0.98 |
| 494 | 0.046 | 0.00652 | 0.78 | 638 | 0.008 | 0.00216 | 0.98 |
| 496 | 0.044 | 0.00631 | 0.78 | 640 | 0.008 | 0.00214 | 0.97 |
| 498 | 0.042 | 0.00615 | 0.78 | 642 | 0.008 | 0.00187 | 0.96 |

(Continued)

TABLE 3 | Continued

| λ | A(λ) | SD | B(λ) | λ | A | SD | B(λ) |
|-----------|----------------|---------|----------------|-----------|-------|---------|----------------|
| 500 | 0.040 | 0.00599 | 0.78 | 644 | 0.008 | 0.00206 | 0.98 |
| 502 | 0.038 | 0.00583 | 0.78 | 646 | 0.008 | 0.00209 | 0.99 |
| 504 | 0.036 | 0.00564 | 0.78 | 648 | 0.008 | 0.0021 | 0.98 |
| 506 | 0.034 | 0.00539 | 0.79 | 650 | 0.008 | 0.00189 | 0.97 |
| 508 | 0.032 | 0.00519 | 0.78 | 652 | 0.008 | 0.00204 | 0.96 |
| 510 | 0.030 | 0.00503 | 0.79 | 654 | 0.008 | 0.00217 | 0.96 |
| 512 | 0.028 | 0.00498 | 0.79 | 656 | 0.008 | 0.00181 | 0.96 |
| 514 | 0.027 | 0.00453 | 0.78 | 658 | 0.009 | 0.0017 | 0.95 |
| 516 | 0.025 | 0.00434 | 0.78 | 660 | 0.010 | 0.00178 | 0.95 |
| 518 | 0.024 | 0.00414 | 0.78 | 662 | 0.012 | 0.00162 | 0.94 |
| 520 | 0.023 | 0.00416 | 0.78 | 664 | 0.013 | 0.00184 | 0.94 |
| 522 | 0.022 | 0.00391 | 0.78 | 666 | 0.016 | 0.00213 | 0.94 |
| 524 | 0.021 | 0.00376 | 0.78 | 668 | 0.018 | 0.00225 | 0.93 |
| 526 | 0.020 | 0.00393 | 0.79 | 670 | 0.020 | 0.00244 | 0.94 |
| 528 | 0.019 | 0.00372 | 0.80 | 672 | 0.022 | 0.00249 | 0.95 |
| 530 | 0.018 | 0.00386 | 0.79 | 674 | 0.024 | 0.00253 | 0.95 |
| 532 | 0.017 | 0.00365 | 0.80 | 676 | 0.024 | 0.00251 | 0.93 |
| 534 | 0.017 | 0.00362 | 0.82 | 678 | 0.024 | 0.00262 | 0.92 |
| 536 | 0.016 | 0.00343 | 0.81 | 680 | 0.024 | 0.00262 | 0.98 |
| 538 | 0.015 | 0.00349 | 0.82 | 682 | 0.022 | 0.00245 | 0.98 |
| 540 | 0.014 | 0.00343 | 0.84 | 684 | 0.020 | 0.00234 | 0.98 |
| 542 | 0.014 | 0.00337 | 0.89 | 686 | 0.017 | 0.00224 | 0.98 |
| | | | | 688 | 0.014 | 0.00195 | 0.98 |
| | | | | 690 | 0.011 | 0.00162 | 0.98 |
| | | | | 692 | 0.009 | 0.00132 | 0.98 |
| | | | | 694 | 0.007 | 0.00112 | 0.98 |
| | | | | 696 | 0.005 | 0.00102 | 0.98 |
| | | | | 698 | 0.004 | 0.00105 | 0.98 |
| | | | | 700 | 0.003 | 0.0011 | 0.98 |

$a_{ph}(\lambda) = A(\lambda) / (Chl-a)B(\lambda)$ and determination coefficients on the log-transformed data r^2 (summer).

was not analyzed, but rough assessment of NPP (share of photoprotective pigments in total weight all pigments) based on dependence of NPP on light intensity (Babin et al., 1996) showed that NPP in UML was ~ 5 times higher in summer in comparison with NPP in winter (Figure 6).

Seasonal phytoplankton succession observed is typical for the deep-water ecosystem of the Black Sea (Georgieva, 1993; Berseneva et al., 2004; Mikaelyan et al., 2005). In general biomass of the phytoplankton consists of Bacillariophyceae, Dinophyceae, and Prymnesiophyceae (presented mainly by coccolithophores). Two-weekly monitoring at fixed stations in the western deep-water part of the Black Sea showed a change in phytoplankton species composition within an year (Berseneva et al., 2004): in general diatoms were dominating in winter and in yearly spring “blooms,” dinoflagellates and coccolithophores were prevailing in the community in summer. Coccolithophores “bloom” in May-June.

Shift in species dominating in phytoplankton community is attributed with changes in size and shape of the cells. Cells size effects on pigment package within the cells which results

in decreasing of $a_{ph}^*(\lambda)$ due to self-shading of pigments within large cells (Morel and Bricaud, 1981; Sosik and Mitchell, 1994; Fujiki and Taguchi, 2002). In different ocean regions variability in the $a_{ph}^*(\lambda)$ was related with change in phytoplankton species composition and cell size (Bricaud et al., 1995; Cleveland, 1995; Millan-Nunez et al., 2004). Package effect caused by cell size is detected by decreasing of $a_{ph}^*(678)$ (Fujiki and Taguchi, 2002) because at shorter wavelengths $a_{ph}^*(\lambda)$ is affected by accessory pigments as well. Values of $a_{ph}^*(678)$ decreased in winter by $\sim 15\%$ compared with summer due to both C/Chl-*a* and phytoplankton variability (Figures 3, 5) although the large diatoms (*Pseudosolenia calcar-avis*) were dominated in phytoplankton community.

The cells of *Pseudosolenia calcar-avis* have cylindrical shape unlike dinoflagellates, cells of which are closer to the ellipsoid. Volume of *Pseudosolenia calcar-avis* cell exceeds ~ 2 orders of magnitude the volume of the dinoflagellates (*Gymnodinium spp*) cells. However, in the case of the cylindrically shaped cells the large volume is not critical for the cell's capacity to absorb

TABLE 4 | Spectral values of the constant obtained when fitting the variations of $a_{ph}(\lambda)$ vs. the (chlorophyll *a* + phaeopigment) concentration (Chl-*a*) to power laws of the form.

| λ | A(λ) | SD | B(λ) | λ | A | SD | B(λ) |
|-----------|----------------|---------|----------------|-----------|--------|---------|----------------|
| 400 | 0.0285 | 0.00521 | 0.89 | 544 | 0.0147 | 0.00266 | 0.96 |
| 402 | 0.0294 | 0.00513 | 0.88 | 546 | 0.0143 | 0.00264 | 0.97 |
| 404 | 0.0306 | 0.00508 | 0.88 | 548 | 0.0137 | 0.00261 | 0.98 |
| 406 | 0.0318 | 0.00508 | 0.87 | 550 | 0.0131 | 0.00255 | 0.99 |
| 408 | 0.0331 | 0.00510 | 0.87 | 552 | 0.0125 | 0.00247 | 1.00 |
| 410 | 0.0343 | 0.00512 | 0.86 | 554 | 0.0118 | 0.00235 | 1.02 |
| 412 | 0.0354 | 0.00518 | 0.86 | 556 | 0.0111 | 0.00222 | 1.02 |
| 414 | 0.0363 | 0.00521 | 0.85 | 558 | 0.0104 | 0.00206 | 1.04 |
| 416 | 0.0371 | 0.00526 | 0.84 | 560 | 0.0097 | 0.00191 | 1.05 |
| 418 | 0.0376 | 0.00528 | 0.84 | 562 | 0.0090 | 0.00178 | 1.06 |
| 420 | 0.0381 | 0.00529 | 0.83 | 564 | 0.0085 | 0.00165 | 1.06 |
| 422 | 0.0386 | 0.00535 | 0.83 | 566 | 0.0080 | 0.00152 | 1.09 |
| 424 | 0.0391 | 0.00539 | 0.83 | 568 | 0.0076 | 0.00141 | 1.12 |
| 426 | 0.0397 | 0.00543 | 0.82 | 570 | 0.0073 | 0.00130 | 1.14 |
| 428 | 0.0405 | 0.00550 | 0.82 | 572 | 0.0070 | 0.00124 | 1.13 |
| 430 | 0.0415 | 0.00559 | 0.82 | 574 | 0.0069 | 0.00119 | 1.12 |
| 432 | 0.0426 | 0.00569 | 0.82 | 576 | 0.0069 | 0.00115 | 1.12 |
| 434 | 0.0436 | 0.00578 | 0.82 | 578 | 0.0069 | 0.00112 | 1.13 |
| 436 | 0.0444 | 0.00583 | 0.82 | 580 | 0.0070 | 0.00110 | 1.12 |
| 438 | 0.0448 | 0.00586 | 0.82 | 582 | 0.0071 | 0.00109 | 1.12 |
| 440 | 0.0448 | 0.00584 | 0.82 | 584 | 0.0072 | 0.00110 | 1.11 |
| 442 | 0.0444 | 0.00578 | 0.82 | 586 | 0.0073 | 0.00110 | 1.08 |
| 444 | 0.0436 | 0.00565 | 0.82 | 588 | 0.0074 | 0.00111 | 1.08 |
| 446 | 0.0426 | 0.00554 | 0.81 | 590 | 0.0075 | 0.00110 | 1.07 |
| 448 | 0.0416 | 0.00541 | 0.81 | 592 | 0.0075 | 0.00110 | 1.08 |
| 450 | 0.0407 | 0.00530 | 0.81 | 594 | 0.0074 | 0.00110 | 1.07 |
| 452 | 0.0400 | 0.00521 | 0.81 | 596 | 0.0073 | 0.00109 | 1.03 |
| 454 | 0.0396 | 0.00514 | 0.80 | 598 | 0.0071 | 0.00107 | 1.02 |
| 456 | 0.0394 | 0.00508 | 0.80 | 600 | 0.0069 | 0.00106 | 1.05 |
| 458 | 0.0393 | 0.00503 | 0.81 | 602 | 0.0068 | 0.00104 | 1.03 |
| 460 | 0.0394 | 0.00501 | 0.80 | 604 | 0.0066 | 0.00102 | 1.04 |
| 462 | 0.0394 | 0.00496 | 0.80 | 606 | 0.0065 | 0.00102 | 1.07 |
| 464 | 0.0394 | 0.00492 | 0.80 | 608 | 0.0065 | 0.00101 | 1.06 |
| 466 | 0.0393 | 0.00485 | 0.80 | 610 | 0.0066 | 0.00101 | 1.07 |
| 468 | 0.0390 | 0.00479 | 0.80 | 612 | 0.0066 | 0.00100 | 1.09 |
| 470 | 0.0386 | 0.00470 | 0.80 | 614 | 0.0067 | 0.00099 | 1.05 |
| 472 | 0.0381 | 0.00459 | 0.80 | 616 | 0.0069 | 0.00099 | 1.07 |
| 474 | 0.0374 | 0.00448 | 0.79 | 618 | 0.0070 | 0.00099 | 1.08 |
| 476 | 0.0366 | 0.00437 | 0.78 | 620 | 0.0071 | 0.00099 | 1.08 |
| 478 | 0.0358 | 0.00425 | 0.78 | 622 | 0.0072 | 0.00100 | 1.07 |
| 480 | 0.0350 | 0.00416 | 0.79 | 624 | 0.0073 | 0.00100 | 1.07 |
| 482 | 0.0341 | 0.00406 | 0.78 | 626 | 0.0074 | 0.00100 | 1.07 |
| 484 | 0.0334 | 0.00399 | 0.78 | 628 | 0.0075 | 0.00000 | 1.06 |
| 486 | 0.0326 | 0.00392 | 0.78 | 630 | 0.0076 | 0.00101 | 1.06 |
| 488 | 0.0319 | 0.00388 | 0.78 | 632 | 0.0077 | 0.00102 | 1.06 |
| 490 | 0.0311 | 0.00385 | 0.79 | 634 | 0.0079 | 0.00103 | 1.06 |
| 492 | 0.0304 | 0.00380 | 0.79 | 636 | 0.0080 | 0.00104 | 1.03 |
| 494 | 0.0296 | 0.00377 | 0.80 | 638 | 0.0080 | 0.00104 | 1.04 |
| 496 | 0.0288 | 0.00371 | 0.80 | 640 | 0.0080 | 0.00104 | 1.05 |
| 498 | 0.0279 | 0.00364 | 0.81 | 642 | 0.0080 | 0.00107 | 1.04 |

(Continued)

TABLE 4 | Continued

| λ | A(λ) | SD | B(λ) | λ | A | SD | B(λ) |
|-----------|----------------|---------|----------------|-----------|--------|---------|----------------|
| 500 | 0.0270 | 0.00355 | 0.81 | 644 | 0.0080 | 0.00107 | 1.02 |
| 502 | 0.0261 | 0.00344 | 0.82 | 646 | 0.0079 | 0.00108 | 1.01 |
| 504 | 0.0252 | 0.00333 | 0.83 | 648 | 0.0078 | 0.00109 | 1.01 |
| 506 | 0.0243 | 0.00321 | 0.84 | 650 | 0.0078 | 0.00107 | 1.02 |
| 508 | 0.0235 | 0.00310 | 0.85 | 652 | 0.0079 | 0.00107 | 1.03 |
| 510 | 0.0227 | 0.00300 | 0.85 | 654 | 0.0082 | 0.00107 | 1.03 |
| 512 | 0.0220 | 0.00290 | 0.86 | 656 | 0.0087 | 0.00109 | 1.05 |
| 514 | 0.0213 | 0.00280 | 0.86 | 658 | 0.0095 | 0.00115 | 1.05 |
| 516 | 0.0206 | 0.00273 | 0.87 | 660 | 0.0106 | 0.00126 | 1.05 |
| 518 | 0.0200 | 0.00267 | 0.87 | 662 | 0.0121 | 0.00142 | 1.05 |
| 520 | 0.0194 | 0.00262 | 0.87 | 664 | 0.0137 | 0.00160 | 1.04 |
| 522 | 0.0189 | 0.00258 | 0.88 | 666 | 0.0156 | 0.00174 | 1.03 |
| 524 | 0.0184 | 0.00254 | 0.89 | 668 | 0.0175 | 0.00188 | 1.02 |
| 526 | 0.0180 | 0.00252 | 0.90 | 670 | 0.0191 | 0.00196 | 1.01 |
| 528 | 0.0176 | 0.00251 | 0.90 | 672 | 0.0203 | 0.00202 | 0.99 |
| 530 | 0.0172 | 0.00251 | 0.92 | 674 | 0.0210 | 0.00202 | 0.98 |
| 532 | 0.0169 | 0.00252 | 0.91 | 676 | 0.0211 | 0.00200 | 0.96 |
| 534 | 0.0165 | 0.00254 | 0.92 | 678 | 0.0206 | 0.00196 | 0.96 |
| 536 | 0.0162 | 0.00257 | 0.93 | 680 | 0.0194 | 0.00188 | 0.95 |
| 538 | 0.0159 | 0.00260 | 0.94 | 682 | 0.0178 | 0.00180 | 0.95 |
| 540 | 0.0155 | 0.00263 | 0.94 | 684 | 0.0156 | 0.00171 | 0.95 |
| 542 | 0.0152 | 0.00266 | 0.95 | 686 | 0.0132 | 0.00160 | 0.95 |
| | | | | 688 | 0.0108 | 0.00147 | 0.95 |
| | | | | 690 | 0.0086 | 0.00131 | 0.95 |
| | | | | 692 | 0.0066 | 0.00114 | 0.95 |
| | | | | 694 | 0.0051 | 0.00097 | 0.95 |
| | | | | 696 | 0.0038 | 0.00083 | 0.95 |
| | | | | 698 | 0.0029 | 0.00070 | 0.95 |
| | | | | 700 | 0.0022 | 0.00062 | 0.95 |

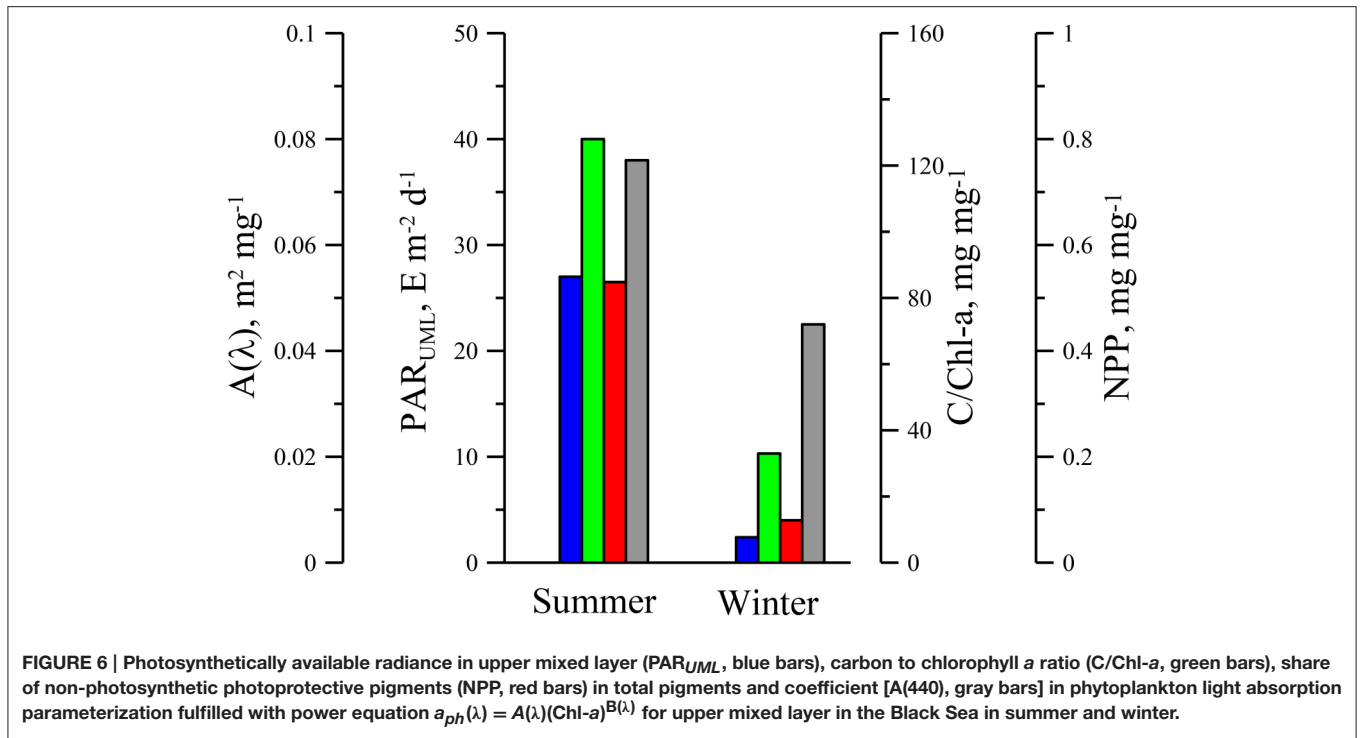
$a_{ph}(\lambda) = A(\lambda) \text{ (Chl-}a\text{)B}(\lambda)$ and determination coefficients on the log-transformed data r^2 (winter).

light. The light absorption capacity of cylindrically shaped cells is determined by the diameter of their section (Kirk, 1976). Therefore, despite the difference in the cell volume optically significant size of cylindrical diatoms (10–30 μm) was similar to that of dinoflagellates (10–40 μm). Consequently, in this case the effect of the size (volume) of the cells on the degree of pigment packaging is not as significant as in the case of large spherical cells (Morel and Bricaud, 1981). It explains weak (~15%) seasonal difference in a_{ph}^* (678) observed in the Black Sea (Figure 5).

CONCLUSIONS

Seasonal differences in chlorophyll-*a* specific phytoplankton light absorption coefficients are caused by annual dynamics in environmental conditions in the (UML) and adaptive response of algae cells/population (via variation of pigment composition and concentration in the cell) and of phytoplankton community (via shift in phytoplankton species composition with attributed changes in size and shape of cell). Consequently, parameterization of the relationship between phytoplankton

light absorption coefficients and chlorophyll *a* concentration proceeded for different seasons (summer and winter) will allow to refine the regional algorithm of Chl-*a* assessment based on remote sensing (Suslin and Churilova, 2016). Because in the Black Sea light absorption by dissolved organic matter there is relatively high and not correlated with phytoplankton absorption or chlorophyll *a* concentration regional Chl-*a* algorithm requires splitting of light absorption into $a_{ph}(\lambda)$ and $a_{CDM}(\lambda)$ (Suslin and Churilova, 2016) and then Chl-*a* is retrieved from the $a_{ph}(\lambda)$ at 490 nm. Relationships between Chl-*a* and $a_{ph}(\lambda)$ obtained for the summer and winter conditions in the Black Sea differ by coefficients A(λ) in power equation, but coefficients B(λ) are practically the same (Figure 5). Consequently, values of A(λ) coefficient define the seasonal difference in retrieval of Chl-*a* based on $a_{ph}(\lambda)$. Values of A(λ) at 490 nm are equal 0.048 and 0.031 $\text{m}^2 \text{mg}^{-1}$ correspondently for summer and winter conditions in UML of the Black Sea (Tables 3, 4). For instance, using the summer relationship between Chl-*a* and summer a_{ph} (490) values one can get Chl-*a* equal to 0.2–0.3 mg m^{-3} , but using the winter link between these parameters or link



obtained for different regions of the world ocean (Bricaud et al., 1995) one gets Chl-*a* equal to 0.36–0.53 or to 0.34–0.55 mg m^{-3} . Consequently, the retrieved Chl-*a* values become almost twice lower if one takes into account the Black Sea summer conditions and relevant relationship between $a_{ph}(\lambda)$ and Chl-*a*. Undoubtedly accuracy of splitting of light absorption into $a_{ph}(\lambda)$ and $a_{CDM}(\lambda)$ also affect the accuracy of Chl-*a* assessment (Suslin and Churilova, 2016).

Moreover, seasonal difference in links between $a_{ph}(\lambda)$ and Chl-*a* could provide more correct assessment of downwelling radiance and primary production in the Black Sea using spectral approaches (Churilova et al., 2016). However, it should be noted that application of the obtained $a_{ph}(\lambda)$ parametrization is limited by the rather narrow range of Chl-*a*, which was measured in the deep waters. The relatively narrow range of Chl-*a* caused the high values of $B(\lambda)$ coefficients in comparison of those obtained based on numerical data measured in different regions of World Ocean with Chl-*a* covering the range 0.02–25 mg m^{-3} (Figure 5; Bricaud et al., 1995).

The parameterization obtained based on bio-optical data measured in deep waters is unlikely to be correct for coastal waters. Coastal waters may differ from deep waters in nutrient availability, transparency and turbulence. These different environmental conditions would result in change of intracellular pigment concentration and phytoplankton species composition which in turn effect on $a_{ph}^*(\lambda)$. In this regard since 2014 bio-optical properties have been investigated in the Crimean coastal waters in different seasons. These new data will be merged with summer results measured before (Churilova and

Berseneva, 2004; Dmitriev et al., 2009) and then analyzed to determine the seasonality in $a_{ph}(\lambda)$ parameterization.

AUTHOR CONTRIBUTIONS

TC, idea, management and writing. VS, mathematical proceeding and interpretation data. OK, contribution to the discussion. TE, chlorophyll and absorption measurements, calculations. NM, chlorophyll and absorption measurements, calculations. VM, phytoplankton data analysis. LS, phytoplankton species identification.

FUNDING

The work presented in this paper was carried out in the framework of RF state task according to plan of scientific research of the AO. Kovalevsky Institute of Marine Biological Research (theme # 0828-2014-0016) and of the Marine Hydrophysical Institute (theme # 0827-2014-0011). The work was partially supported by RFBR (project 17-05-00113).

ACKNOWLEDGMENTS

The authors are very thankful to ESA and PML for invitation us to attend the workshop “Color and Light in the Ocean (CLEO)” held at ESRIN, Frascati, Italy on 6-8 September, 2016. The authors would like to thank the reviewers for their helpful and constructive comments that greatly contributed to improving the paper. The authors thank very much ESA for covering of the article processing charges.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

The reviewer BB and handling Editor declared their shared affiliation, and the handling Editor states that the process nevertheless met the standards of a fair and objective review.

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