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SPECTRAL BIO-OPTICAL PROPERTIES OF WATER OF ATLANTIC SECTOR OF ANTARCTIC

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Studies of variability of spectral bio-optical properties of water of Atlantic sector of Antarctic were carried out during the 79[th] cruise of the RV "Akademik Mstislav Keldysh" (11.01.2020–04.02.2020). Chlorophyll *a* and phaeopigment concentration varied in the layer studied from 0.1 to 1.8 mg·m^{-3}, except for two stations with content reaching 2.2 and 4.4 mg·m^{-3}. The relationship was revealed between light absorption coefficient by phytoplankton and chlorophyll *a* concentration at a wavelength, corresponding to spectrum maxima: $a_{ph}(438) = 0.044 \times C_a^{1.2}$, $r^2 = 0.84$ ($n = 117$); $a_{ph}(678) = 0.021 \times C_a^{1.1}$, $r^2 = 0.89$ ($n = 117$). Spectral distribution of light absorption coefficient by non-algal particles and colored dissolved organic matter was described by exponential function. Absorption parameterization coefficients were retrieved: (1) light absorption coefficient by non-algal particles (0.001–0.027 m^{-1}) and by colored dissolved organic matter (0.016–0.19 m^{-1}) at a wavelength of 438 nm; (2) spectral slope coefficients of these components (0.005–0.016 and 0.009–0.022 nm^{-1}, respectively).

Keywords: chlorophyll *a*, spectral light absorption coefficient, phytoplankton, non-algal particles, colored dissolved organic matter, Antarctic

The study of spectral bio-optical properties of water is necessary for understanding the regularities of the formation of optical signal, recorded by satellite scanners, and for solving the problem of retrieving water biological characteristics, based on Earth remote sensing data from space (IOCCG. Uncertainties in Ocean…, 2019). Spectral optical properties of suspended and dissolved organic matter in water, *i. e.* their capacity to scatter light and, to a greater extent, to absorb it, are determined by the formation of a light field in the sea, as well as water leaving radiance, recorded by satellite optical scanners (Kirk, 2011 ; Reynolds et al., 2001). For the correct transformation of satellite data (remote sensing reflectance Rrs) into water quality and productivity indicators, regional algorithms are required. These algorithms must be developed on the basis of empirical regularities of variability of spectral light absorption coefficient by phytoplankton pigments, non-algal particles, and colored dissolved organic matter, as well as their relationship with concentration of chlorophyll *a* (the main photosynthetic pigment).

The studies of Antarctic water, aimed at understanding the effect of the content of optically active components of the environment and their spectral properties on the formation of a signal, "visible" for remote scanners, have evolved from relatively simple ones, based on the analysis of relationships between chlorophyll *a* concentration and spectral coefficients of light attenuation, as well as remote sensing reflectance (Dierssen & Smith, 2000 ; Figueroa, 2002 ; Mitchell & Holm-Hansen, 1991), to comprehensive ones: analysis of spectral absorption and scattering coefficients by all optically active components (Ferreira et al., 2018, 2017). To date, only single complex researches are known (Ferreira et al., 2018, 2017), carried out in the water area west of the Antarctic Peninsula.

In this regard, the aim of our work was to study the variability of spectral light absorption coefficients by suspended and dissolved organic matter in water of Atlantic sector of Antarctic in summer, based on the results, obtained in the research cruise (11.01.2020–04.02.2020).

MATERIAL AND METHODS

The studies were carried out during the 79th cruise of the RV "Akademik Mstislav Keldysh" in water of Atlantic sector of Antarctic from 11.01.2020 to 04.02.2020. Most stations were carried out in the Bransfield Strait (Fig. 1A) and in the Powell Basin (Fig. 1B).

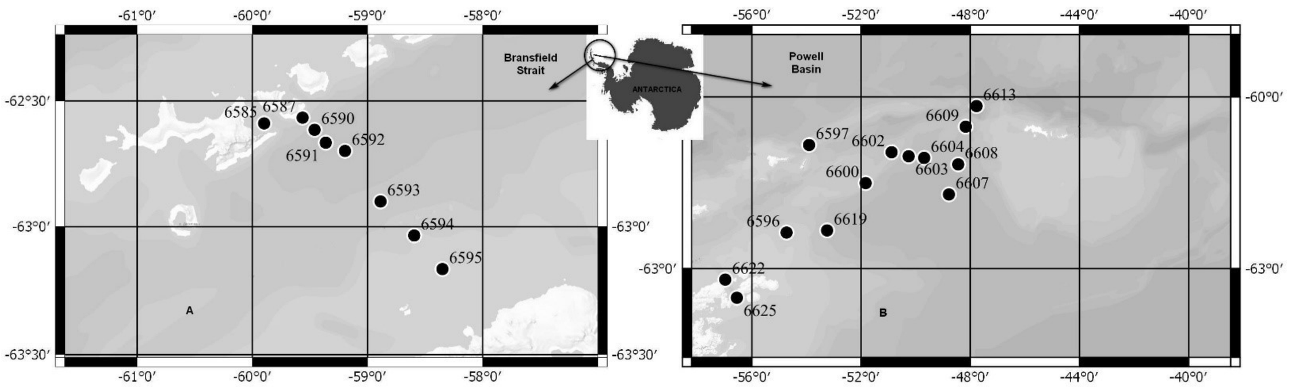

Fig. 1. Map of stations (●) of bio-optical studies, carried out in the 79th cruise of the RV "Akademik Mstislav Keldysh" in the Bransfield Strait (A) and the Powell Basin (B) (11.01.2020–04.02.2020)

The measurement of photosynthetically active radiation (hereinafter PAR), falling on the sea surface, and of its change with a depth of up to 100 m was carried out using Li-Cor deck and submersible devices. Vertical profiles of changes in temperature and chlorophyll *a* fluorescence intensity were recorded by a PUM-200 transparent probe. Samples were taken by a cassette of bathometers at the horizons, selected on the basis of the measured profiles of hydrophysical indicators.

Euphotic zone depth Z_{eu} was taken to be equal to penetration depth of 1 % of PAR, falling on the sea surface.

Chlorophyll *a* and phaeopigment concentration C_a was determined by the standard spectrophotometric method (Jeffrey & Humphrey, 1975 ; Lorenzen, 1967). Water samples (1.5–2 L) were filtered through glass microfiber filters (GF/F, Whatman) at low vacuum (< 0.2 atm). The filters were foil-wrapped and stored in liquid nitrogen in a cryogenic storage dewar, until measurements in the laboratory were carried out.

Light absorption by suspended matter $a_p(\lambda)$ was measured according to the NASA protocol (IOCCG. Ocean Optics…, 2019). Optical densities were measured at a wavelength range 350–750 nm with a step of 1 nm by a double-beam spectrophotometer Lambda 35 (PerkinElmer), equipped with an integrating sphere. The division of $a_p(\lambda)$ into light absorption by phytoplankton pigments $a_{ph}(\lambda)$ and by non-algal particles $a_{NAP}(\lambda)$ was carried out according to (Kishino et al., 1985). Absorption correction (β-correction) was performed in line with (Mitchell, 1990). Correction for non-specific absorption was made by "zeroing" by the mean value for 700–750 nm.

Light absorption of colored dissolved organic matter $a_{CDOM}(\lambda)$ was measured according to the NASA protocol (IOCCG. Ocean Optics…, 2019). Water samples were filtered through a nucleopore filter (Sartorius, 0.2 μm), previously rinsed with deionized water. For prefiltration, GF/F filters were used. Optical densities were measured at a wavelength range 250–750 nm with a step of 1 nm by a spectrophotometer Lambda 35.

Spectral distribution of $a_{NAP}(\lambda)$ and $a_{CDOM}(\lambda)$ was parameterized. Thus, the data were fitted to exponential function at the spectral ranges 400–700 and 350–500 nm, respectively:

$$a_i(\lambda) = a_i(\lambda_{ref}) \times e^{-S_i \times (\lambda - \lambda_{ref})}\ , \tag{1}$$

where i is non-algal particles (NAP) or colored dissolved organic matter (CDOM);

λ_{ref} is reference wavelength (in our case, λ_{ref} = 438 nm);

S_i is spectral slope coefficient, nm^{-1}.

RESULTS

During the study period, surface temperature in the Bransfield Strait varied from −0.47 to +3.2 °C, averaging +1.3 °C. In the Powell Basin, it varied from −0.77 to +2.0 °C, averaging +0.72 °C.

In the study area, high non-uniformity in water hydrological structure was noted (Fig. 2). At most stations, the temperature was almost equal within the layer studied. At single stations (6591, 6592, and 6593), an upper mixed layer with a thickness of 7–47 m was formed. The complicity and non-uniformity of water hydrological structure was accompanied by a similar non-uniformity in the vertical profile of chlorophyll *a* fluorescence (Fig. 2).

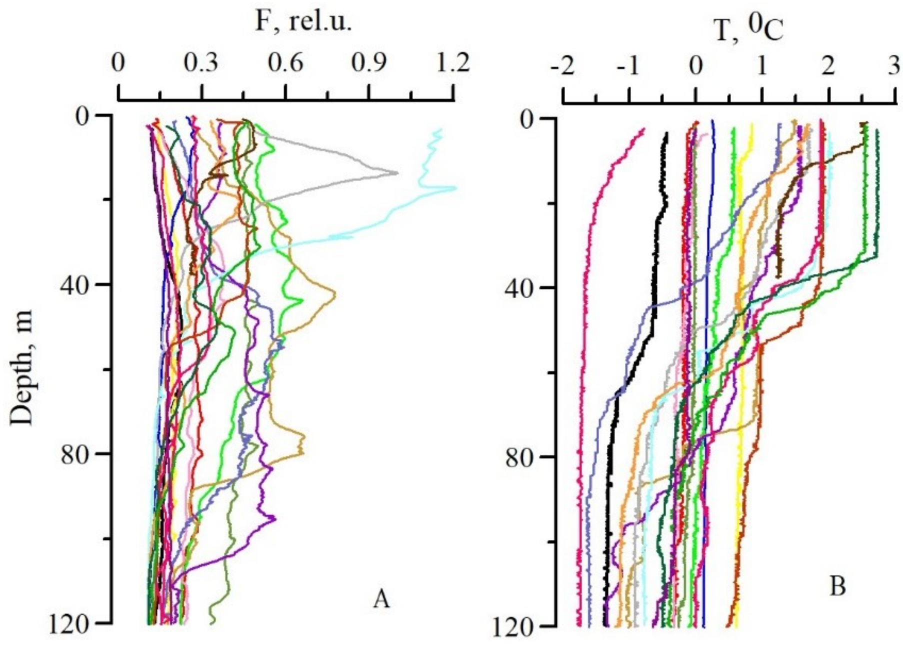

Fig. 2. Vertical profiles (n = 26) of chlorophyll *a* fluorescence intensity (A) and water temperature (B) of Atlantic sector of Antarctic (11.01.2020–04.02.2020)

Euphotic zone depth varied between stations in a narrow range: from 50 m (st. 6614) to 83 m (st. 6619), except for two stations (st. 6609 and 6613), where lower water transparency was registered. On these stations, Z_{eu} was of 28 and 35 m, respectively. On average, Z_{eu} was of (64 ± 12) m.

An important indicator of water productivity and quality is concentration of chlorophyll *a* as the main photosynthetic pigment.

Chlorophyll *a* and phaeopigment concentration in the surface layer in the study area – the Bransfield Strait and the Powell Basin – changed significantly: from 0.25 to 4.4 mg·m^{-3} (Fig. 3A). The maximum values were obtained at st. 6609 (C_a = 4.4 mg·m^{-3}) and st. 6613 (C_a = 2.2 mg·m^{-3}) in the Powell Basin. In this case, the mean C_a value in the surface layer for all stations, except for st. 6609 and 6613, was (0.72 ± 0.35) mg·m^{-3}. Within the euphotic layer, C_a values varied from 0.1 to 1.8 mg·m^{-3}, except for st. 6609 and 6613. For the whole layer, C_a averaged (0.61 ± 0.35) mg·m^{-3}.

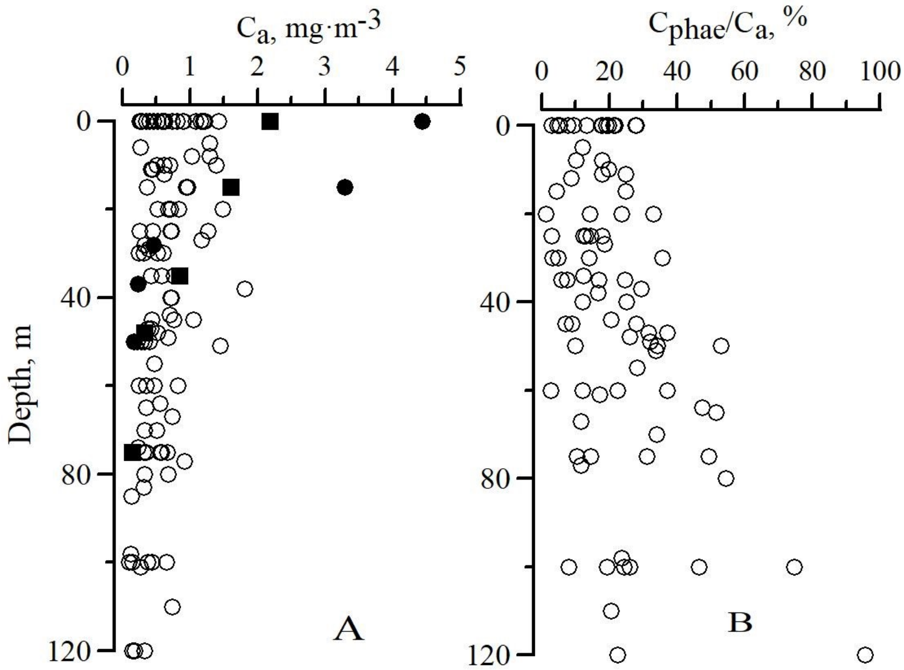

Fig. 3. Vertical profiles of chlorophyll *a* and phaeopigment concentration (C_a) at st. 6609 (●), at st. 6613 (■), and at other stations (○) (A); vertical profiles of relative phaeopigment concentration (C_{phae}/C_a) (B) in water of Atlantic sector of Antarctic (11.01.2020–04.02.2020)

There are three types of C_a vertical distribution (Fig. 4):

1) uniform C_a distribution within the euphotic layer (for example, at st. 6602);
2) with a maximum of C_a in the lower euphotic layer (~ 1–0.1 % PAR) (for example, at st. 6604);
3) C_a decrease with depth within the layer studied (for example, at st. 6614).

Profiles of the third type, characterized by C_a decrease with depth, were the most common ones. They were registered at 16 stations out of 26.

Phaeopigment ratio in chlorophyll *a* and phaeopigment concentration varied from 1 to 96 %, averaging (22 ± 16) % (Fig. 3B). The maximum values (47–96 %) were registered in the layer deeper than 50 m. In the upper, lighted layer (0 to 50 m), phaeopigment ratio did not exceed 30 %. This indicates a good physiological state of phytoplankton in this layer.

In the study area, high variability of spectral coefficients $a_{ph}(\lambda)$ and $a_{NAP}(\lambda)$ was recorded (Fig. 5).

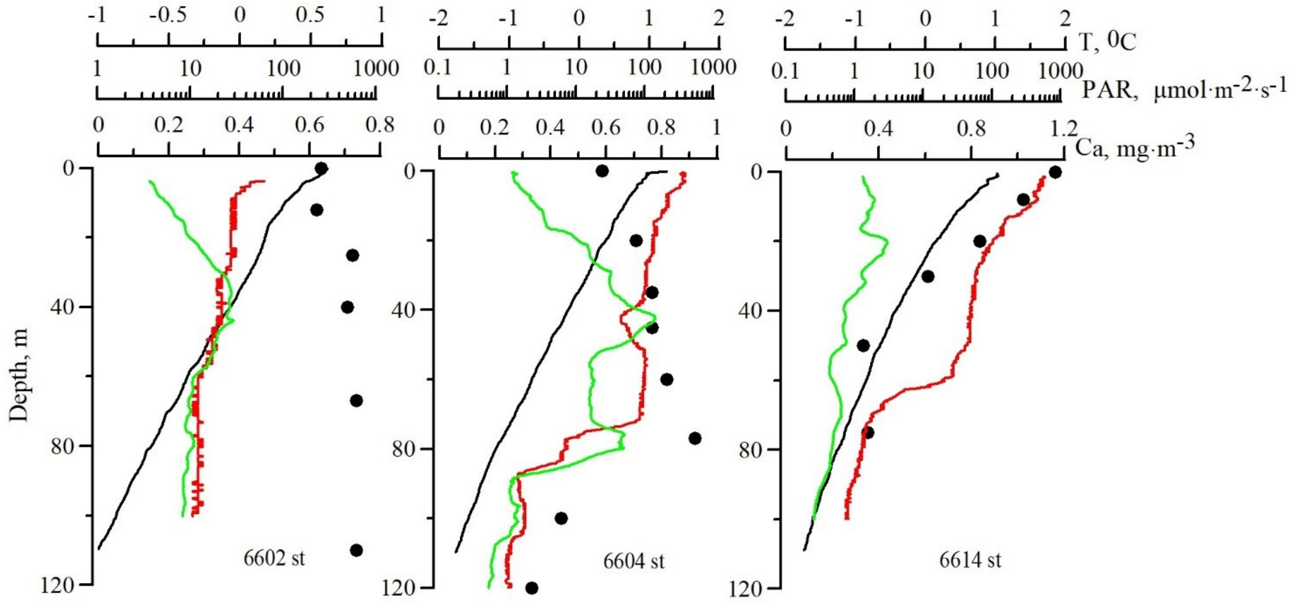

Fig. 4. Examples of typical vertical profiles of temperature (T, red line), chlorophyll *a* fluorescence intensity (F, green line), photosynthetically active radiation (PAR, black line), and chlorophyll *a* and phaeophytin concentration (C_a, ●) at single stations in water of Atlantic sector of Antarctic (11.01.2020–04.02.2020)

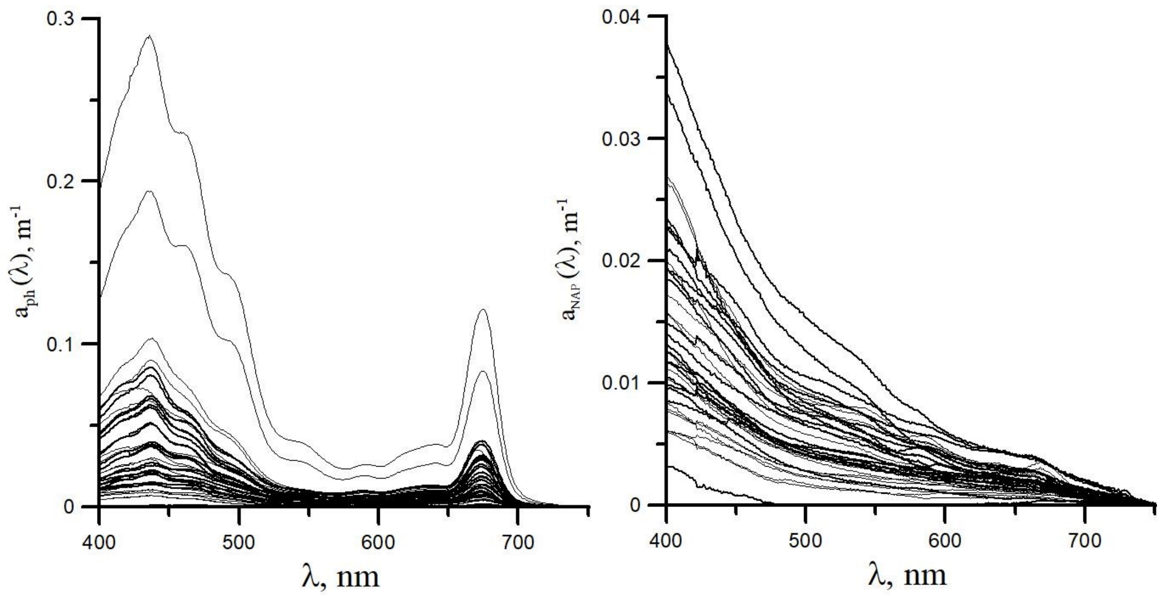

Fig. 5. Light absorption spectra of phytoplankton pigments $a_{ph}(\lambda)$ and non-algal particles $a_{NAP}(\lambda)$ in water of Atlantic sector of Antarctic (11.01.2020–04.02.2020)

The $a_{ph}(\lambda)$ spectra have two main absorption maxima: in the blue and red spectral domains (at ~ 438 and ~ 678 nm, respectively). For the entire data array, the ratio between the coefficients in these spectra peaks (R) varied in a range 1.1–2.8, with a trend towards a decrease with depth. R value varied from 2.8–2.3 in the surface layer to 2.1–1.1 in the end of the layer studied. Values in the blue [$a_{ph}(438)$] and red [$a_{ph}(678)$] maxima varied 0.001–0.29 and 0.001–0.12 m^{-1}, respectively. The highest values were recorded at the stations with high chlorophyll *a* concentration (st. 6609 and 6613), the lowest ones – in the lower euphotic layer.

A relationship was established between C_a and $a_{ph}(\lambda)$ at single wavelengths, corresponding to the spectrum maxima: $a_{ph}(438)$ and $a_{ph}(678)$ (Fig. 6).

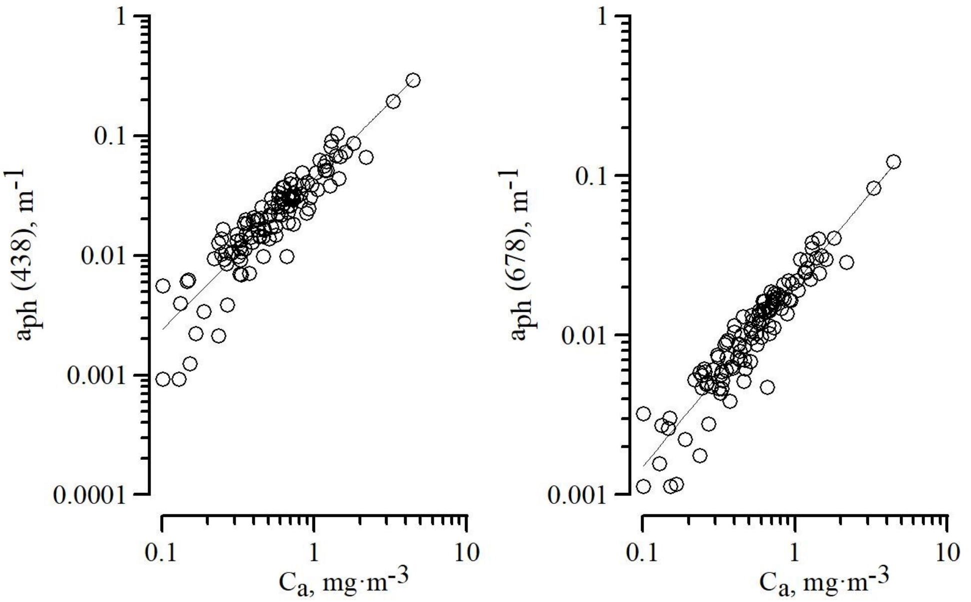

Fig. 6. Dependence of light absorption coefficient by phytoplankton pigments at wavelengths of 438 nm [$a_{ph}(438)$] and 678 nm [$a_{ph}(678)$] on chlorophyll *a* and phaeopigment concentration (C_a) in water of Atlantic sector of Antarctic (11.01.2020–04.02.2020)

These relationships are described by exponential functions with high coefficients of determination:

$$a_{ph}(438) = 0.044 \times C_a^{1.2}, r^2 = 0.84, n = 117\ , \tag{2}$$

$$a_{ph}(678) = 0.021 \times C_a^{1.1}, r^2 = 0.89, n = 117\ . \tag{3}$$

Light absorption coefficients at a wavelength of 438 nm by non-algal particles [a_{NAP} *(438)*] and colored dissolved organic matter [a_{CDOM} *(438)*] varied from 0.001 to 0.027 m^{-1} and from 0.016 to 0.19 m^{-1}, respectively. Spectral slope coefficients S_{NAP} and S_{CDOM} ranged 0.005–0.016 nm^{-1} and 0.009–0.022 nm^{-1}, respectively. The mean values were (0.010 ± 0.002) nm^{-1} for S_{NAP} and (0.013 ± 0.003) nm^{-1} for S_{CDOM}.

For the surface layer (0–1 m), relative contribution of all optically active components to total light absorption coefficients at 438 nm was estimated. The largest one was made by colored dissolved organic matter: from 6 to 88 %, averaging (54 ± 22) %. Phytoplankton contribution was smaller: from 7 to 78 %, averaging (36 ± 19) %. The smallest one was registered for non-algal particles: from 4 to 20 %, averaging (10 ± 5) %.

DISCUSSION

During the study period, different types of vertical profiles of chlorophyll *a* fluorescence were registered (see Fig. 2): uniform distribution; profiles with maximum at different depths; and fluorescence decrease with depth. This is probably associated with vertical distribution of water temperature and density. Similar types of distribution of chlorophyll *a* fluorescence were recorded earlier in Antarctic Peninsula water (Figueiras et al., 1999).

The depth of the euphotic zone was comparable to that of the upper mixed layer, except for several stations, where temperature stratification of water within the euphotic zone was recorded (see Fig. 2). The shape of $a_{ph}(\lambda)$ spectrum reflects cell pigment composition, which, in turn, depends on phytoplankton species composition (Churilova et al., 2008 ; Ciotti et al., 2002 ; Morel & Bricaud, 1981). Chlorophyll-*a*-specific light absorption coefficient by phytoplankton pigments is determined by intracellular pigment content, as well as by shape and size of phytoplankton cells (Bricaud et al., 1995 ; Morel & Bricaud, 1981).

The exponential functions obtained, reflecting the relationship between light absorption coefficient by phytoplankton pigments at 438 and 678 nm and chlorophyll *a* and phaeopigment concentration, can help in calculating $a_{ph}(438)$ and $a_{ph}(678)$ on the basis of C_a data. In these equations, the power coefficient is higher than 1. This indicates a slight increase in C_a-specific absorption coefficients with increase in C_a content in water, which reflects a decrease in the degree of pigment packing in phytoplankton cells (Morel & Bricaud, 1981). This is probably due to the fact that in more trophic water, *i. e.* with higher C_a values, phytoplankton is represented by smaller cell species.

The $a_{ph}(\lambda)$ spectra in the lower euphotic zone (at penetration depth of 1–0.1 % of PAR) were smoother than in the upper one, with minimum R values registered. In the blue spectral domain, accessory pigments and chlorophyll *a* absorb light (Phytoplankton Pigments in Oceanography…, 1997). The red maximum of the spectrum (at 678 nm) is formed due to light absorption by chlorophyll *a* and phaeopigments. A decrease in R value with depth indicates a decrease in the ratio of accessory pigments relative to chlorophyll *a* concentration.

At all stations, except for st. 6609 (at depths of 0 and 15 m), in the obtained light absorption spectra by phytoplankton pigments, no local maximum was registered at a wavelength of 544 nm, corresponding to phycoerythrin absorption band (Ting et al., 2002).

Our values of a_{NAP} *(438)*, a_{CDOM} *(438)*, S_{NAP}, and S_{CDOM} corresponded to those recorded earlier in Antarctic Peninsula water (Ferreira et al., 2018). They were also similar to those registered for the Black Sea in winter (Churilova et al., 2017).

Relative contributions of optically active components of the environment to total light absorption in the surface layer are not the same. Thus, light was mostly absorbed by non-algal component. It is planned to carry out a detailed analysis of the factors, affecting the ratio between all optically active components, in order to use it in development of a refined algorithm for C_a recovery by satellite data.

The data array obtained makes it possible to analyze the variability of absorption coefficients depending on the hydrophysical and hydrochemical conditions in the environment. Moreover, the data array makes it possible to identify regularities that can be helpful in further works on studying the effect of suspended and dissolved organic matter on spectral properties of PAR in the sea, as well as on studying phytoplankton capacity to use it in the photosynthesis. These regularities can also be helpful in research on modeling water quality and productivity indicators, based on Earth remote sensing data from space.

Conclusions:

1. New data were obtained on the variability of chlorophyll *a* and phaeopigment concentration and spectral light absorption coefficients by all optically active components of the environment in the Bransfield Strait and the Powell Basin.
2. Non-uniformity in vertical distribution of chlorophyll *a* concentration was registered. High variability (of more than an order of magnitude) of spectral light absorption coefficient by phytoplankton pigments, non-algal particles, and colored dissolved organic matter was recorded.

3. Parameterization of light absorption by suspended and dissolved matter was performed. By the coefficients obtained, it is possible to recover light absorption spectra by these components.

This work has been carried out within the framework of IBSS government research assignments "Study of the spatiotemporal organization of aquatic and terrestrial ecosystems in order to develop an operational monitoring system, based on remote sensing data and GIS technologies" (No. AAAA-A19-119061190081-9) and "Comprehensive studies of the current state of the ecosystem of the Atlantic sector of the Antarctic" (No. AAAA-A19-119100290162-0), as well as with the support of government research assignment No. 0128-2019-0008. Optical data analysis was carried out with the support of the RFBR grant No. 19-55-45024 ИНД_а.

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СПЕКТРАЛЬНЫЕ БИООПТИЧЕСКИЕ ПОКАЗАТЕЛИ ВОД АТЛАНТИЧЕСКОГО СЕКТОРА АНТАРКТИКИ

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Исследования изменчивости спектральных биооптических показателей вод Атлантического сектора Антарктики проводили в 79-м рейсе НИС «Академик Мстислав Келдыш» в период с 11.01.2020 по 04.02.2020. Получено, что концентрация хлорофилла *a* в сумме с феопигментами изменялась в исследованном слое на большинстве станций от 0,1 до 1,8 мг·м$^{-3}$, за исключением двух станций, где достигала 2,2 и 4,4 мг·м$^{-3}$. Установлена связь показателей поглощения света пигментами фитопланктона с концентрацией хлорофилла *a* на длинах волн, соответствующих основным максимумам спектра: $a_{ph}(438) = 0{,}044 \times C_a^{1,2}$, $r^2 = 0{,}84$ ($n = 117$); $a_{ph}(678) = 0{,}021 \times C_a^{1,1}$, $r^2 = 0{,}89$ ($n = 117$). Спектры показателей поглощения света неживым взвешенным веществом и окрашенным растворённым органическим веществом описаны экспоненциальной зависимостью. Подобраны коэффициенты параметризации: (1) показатели поглощения света неживым взвешенным (0,001–0,027 м$^{-1}$) и растворённым органическим веществом (0,016–0,19 м$^{-1}$) на длине волны 438 нм; (2) коэффициенты наклона экспоненты спектров этих компонент (0,005–0,016 и 0,009–0,022 нм$^{-1}$ соответственно).

Ключевые слова: хлорофилл *a*, спектральный показатель поглощения света, фитопланктон, неживое взвешенное вещество, окрашенное растворённое органическое вещество, Антарктида