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DAILY DYNAMICS OF POLYPHENOL ACCUMULATION IN CELLS OF *FUCUS VESICULOSUS* L. AND *ASCOPHYLLUM NODOSUM* (L.) LE JOLIS DURING THE POLAR DAY ON THE BARENTS SEA COAST

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Polyphenols are a group of secondary metabolites that protect the organism from ultraviolet radiation, participate in plant metabolism, and also have therapeutic properties. Studying the dynamics of polyphenol accumulation in brown algae (Phaeophyceae: Fucales) is of considerable interest for understanding the mechanisms of their adaptation to changing environment. The aim of the work is to reveal daily changes in polyphenol content in cells of *Fucus vesiculosus* Linnaeus and *Ascophyllum nodosum* (Linnaeus) Le Jolis inhabiting the Barents Sea coast, to analyze the dependence of their accumulation on light and temperature, and to determine the role of endogenous rhythms and external factors in the regulation of polyphenol metabolism in cells. The study was carried out in July 2022 and 2023 on the Barents Sea coast (both in the natural environment and in a laboratory). The Folin–Ciocalteu spectrophotometric method was used to analyze polyphenol content. The significant daily dynamics of polyphenols was shown. The key changes in their content occur in the natural environment: during the daytime and during low tide, when thalli dry out. During high tide, when thalli are submerged, the concentration of polyphenols does not change. Polyphenol content depends on a combination of light level, temperature, and cycles of drying and submersion. In a laboratory, the daily rhythm of changes in polyphenol concentration is not preserved, which may indicate a reduced role of endogenous rhythms and the predominant role of environmental factors in the regulation of polyphenol synthesis. The data obtained expand information on Fucales physiological and biochemical features in the Arctic zone, as well as on mechanisms of algal adaptation to the tidal zone of seas. The results can be used in the development of algae aquaculture technology to obtain raw materials with desired properties.

Keywords: polyphenols, Fucales, temperature, light conditions, tidal cycle, polar day, Barents Sea

Polyphenols are secondary metabolites in different groups of algae [Mezghani et al., 2016], which perform a wide range of functions in a plant: from formation of cell walls and protection against excess UV radiation [Arnold, Targett, 1998, 2000; Pavia, Toth, 2000; Schoenwaelder, 2002; Schoenwaelder, Clayton, 1999; Steinberg, 1988, 1995; Van Alstyne et al., 1999] to participation in regeneration processes in damaged fragments of a thallus [Ryzhik, Fisak, 2018] and in mechanisms of plant protection from being consumed by hydrobionts [Dubois, Iken, 2012]. Phlorotannins are the most common group of polyphenols in brown algae; quite often, these two terms are used as synonyms in scientific literature on brown algae [Arnold, Targett, 1998; Jormalainen et al., 2003]. In cells, they both occur in a bound form (as a component of cell walls) and in a soluble one. Soluble polyphenols are contained in physodes: special structures typical for brown algae only. In a thallus, those are usually localized in the cortical cell layer and in intermediate one [Schoenwaelder, 2002].

Polyphenol content in marine algae depends on both internal and external factors [Reboleira et al., 2021]. The internal ones are: processes of the life cycle [Van Alstyne et al., 2001], *inter alia* algal reproduction [Ragan, Jensen, 1978]; the localization of the site; and the age of a tissue/thallus [Pedersen, 1984]. Many works analyze effects of various external factors on polyphenol accumulation; for example, papers investigate effects of salinity [Ragan, Glombitza, 1986], availability of biogenic elements [Peckol et al., 1996], and consuming by phytophages [Pavia et al., 1997].

For algae, the presence of seasonal and diurnal fluctuations in various functional indicators has been established; those include variations in physiological activity, photosynthetic pigment content, and polyphenol concentration. Such fluctuations allow macrophytes to successfully inhabit various environments remaining viable. The seasonal dynamics in polyphenol accumulation depends on both the species specificity and climatic characteristics of the region [Connan, 2004; Connan et al., 2006; Jennings, Steinberg, 1997; Ryzhik, Fisak, 2018; Tkach, Obluchinskaya, 2017]. Circadian rhythms are also important, especially for algae in a littoral zone (due to its instability). Homeostasis is maintained by the interaction of endogenous rhythms and mechanisms involved in formation of rapid responses of an organism to changing external conditions.

For seasonal rhythms in macrophytes, clear photoperiodic reactions have been identified: the ones manifesting themselves in fluctuations in physiological activity and in accumulation of certain substances contributing to increasing resistance (for example, to cold). Daily reactions have been studied to a lesser extent. Previously, researchers determined daily dynamics of metabolic activity, activity of antioxidant enzymes, accumulation of free amino acids and polyphenols, rhythms of cell division, sporogenesis, *etc.* [Connan, 2004; Klindukh et al., 2023; Ryzhik, 2016]. However, we still do not know: is the cause of these changes rooted in endogenous rhythms or in a reaction to varying effect of a factor? Studies on the dynamics in accumulation of polyphenols for 24 h and more allow revealing features of fluctuations in their concentration, as well as aspects of regulation of this process (specifically, the role of endogenous rhythms). Importantly, macrophyte sampling from one site reduces the effect of local conditions in the habitat. We can compare our results with those of similar surveys that covered other areas, and this helps in revealing the universal nature of investigated changes. Having complete data on mechanisms that contribute to growth of marine algae in a littoral zone facilitates our understanding of the evolution of marine macrophyte populations in particular and biocenoses in general in a changing climate [Abdala-Díaz et al., 2006; Connan et al., 2004].

We aimed at revealing diurnal changes in the content of polyphenols in cells of *Fucus vesiculosus* Linnaeus, 1753 and *Ascophyllum nodosum* (Linnaeus) Le Jolis, 1863 (Phaeophyceae: Fucales) inhabiting the Barents Sea coastline. Also, we aimed at analyzing a dependence in their accumulation on light level and temperature, and at determining the role of endogenous rhythms and external factors in regulation of polyphenol metabolism in brown algae.

Data obtained will deepen the understanding of the metabolism regulation and its dependence on internal and external factors, and also contribute to revealing mechanisms of algal adaptation to habitat conditions in a littoral zone. Since polyphenols feature antioxidant, antiviral, and anti-inflammatory activity and are used in the composition of therapeutic and prophylactic agents in the food and pharmaceutical industries, it is necessary to analyze the key aspects in their accumulation: daily dynamics, environmental factors, *etc.* [Aminina et al., 2020; Bogolitsyn et al., 2018]. The results will help in obtaining valuable raw materials by adjusting the period and time of macrophyte extraction, as well as in developing technology of algal cultivation.

MATERIAL AND METHODS

Algae were sampled on the Murmansk coast of the Barents Sea in Dalniye Zelentsy vicinity (N68°97′, E33°08′) in July 2022 and 2023. Apexes of *F. vesiculosus* and *A. nodosum* thalli were analyzed.

When identifying species, we followed a field atlas [Rasteniya i lishainiki, 2016].

In a laboratory, thalli were cleaned from epiphytes, and apexes of thalli of not more than 1 cm were cut. Algae were fixed in liquid nitrogen within 10 min after sampling.

Four variants of experiment were carried out to measure polyphenol concentration in *F. vesiculosus* and *A. nodosum* cells.

Fucus vesiculosus. **Variant 1:** algae were sampled in a littoral zone every 2 h for 24 h (on 14–15 July, 2022). **Variant 2:** algae were sampled in a littoral zone every 2 h for 12 h (on 6 July, 2023). Sampling cycle was as follows: high tide – low tide – high tide. **Variant 3:** algae were sampled in a littoral zone every 2 h for 12 h (on 13 July, 2023). Sampling cycle was as follows: low tide – high tide – low tide.

To reveal the features of polyphenol accumulation under stable conditions, algae were acclimated for 3 days and then sampled according to the scheme of variants 2 and 3. Laboratory conditions were as follows: temperature-controlled chamber, photoperiod 24 h : 0 h (light : darkness), water temperature +10 °C, air temperature +8 °C, light level (photosynthetically active radiation) 1,200 mmol·m^{-2}·s^{-1}, and constant water mixing. This part of the experiment was carried out to determine endogenous rhythms in regulation of polyphenol accumulation, and also to clarify effects of temperature and illuminance on the content of these metabolites.

Ascophyllum nodosum. A scheme of **variant 4** was similar to that of variant 2: algae were sampled every 2 h for 12 h (on 12 July, 2023). Sampling cycle was as follows: low tide – high tide – low tide. In this variant, there was no comparison with macrophytes in a laboratory.

During sampling (every 2 h), light level was measured with a LI-185 quantum/radiometer/photometer (LI-COR Biosciences, the USA). A phase of a tidal cycle was recorded (based on high- and low-tide tables calculated with WXTide32 free software, https://www.wxtide32.com/download.html). Environmental temperature (during high tide, it was water temperature, as algae were submerged; during low tide, it was air temperature) was measured with a mercury thermometer TL-4 (Russia) (technical specifications TU 25-2021.003-88). Also, cloud cover was recorded.

Polyphenol content was determined in cells of thallus apex according to a standard method of Folin–Ciocalteu [Jormalainen et al., 2003; Koivikko et al., 2005].

Samples were preliminary ground in a porcelain mortar using liquid nitrogen. Extraction was carried out 3 times with 96% ethanol. Samples were centrifuged at 12,000 g for 10 min. Supernatants were united.

To carry out the reaction, 1.0 mL of a sample aliquot was mixed in a test tube with 1.0 mL of 1N Folin–Ciocalteu reagent (PanReac AppliChem, India). After 3 min, 2.0 mL of Na_2CO_3 saturated solution was added to the mixture. Samples were incubated in the dark at room temperature for 1 h and centrifuged for 8 min (1,600 g). Then, the absorption of supernatant was measured at 730 nm at a PE-5400VI spectrophotometer (Ecroskhim, Russia).

Calculations were made using a calibration curve constructed involving phloroglucinol (1,3,5-trihydroxybenzene, Sigma, Saint Quentin Fallavier, France). The total content of polyphenols was determined *per* 1 g of dry weight of algae.

All the measurements were carried out in three biological and analytical replicates.

To determine the content of dry matter in algal samples, we first removed condensed moisture from the surface. Then, we weighted apexes of thalli on laboratory technical electronic scales VLTE-310 (Gosmetr, Russia) (accuracy of 0.001g), dried in a drying cabinet ShS-80-01 SPU (Russia) for 24 h to constant weight at +105 °C, and re-weighted. The relative dry matter content was found as the ratio of the sample dry weight to its wet weight.

One-way analysis of variance (ANOVA) was carried out to reveal environmental factors that could affect polyphenol content. Based on its results, the presence of a correlation was determined between the factors and polyphenol concentration applying the Spearman's rank correlation coefficient ($p < 0.05$). The results were statistically analyzed in MS Office Excel 2010 and NCSS 11 Statistical Software (NCSS, LLC, https://statsoftstatistica.ru/).

RESULTS

In **variant 1**, daily dynamics of *F. vesiculosus* polyphenols was investigated. The meteorological conditions were as follows. Our observations covered the polar day. Light level varied within 20–1,600 mmol·m^{-2}·s^{-1}. The weather was mostly sunny and cloudless; during measurements from 13:00 to 15:00, it was partly cloudy.

In the daytime, air temperature was +15…+27.8 °C; at night, it was +10…+12 °C. Temperature of the surface water layer (10–15 cm) was +10…+11 °C within 24 h.

Water salinity during high tide, when the alga was submerged, was 35 ‰.

Analysis of polyphenol content within 24 h revealed the curve with one peak occurring at 17:00. Polyphenol concentration decreased by night and remained at the same level during night hours (Fig. 1).

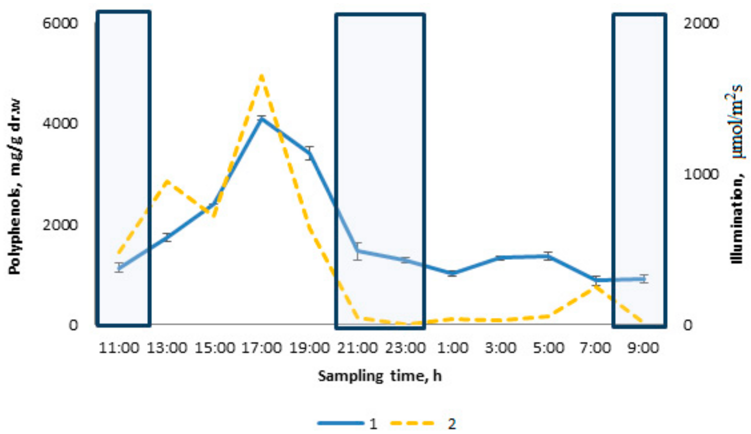

Fig. 1. Dynamics of polyphenol accumulation (1) in *Fucus vesiculosus* cells and illuminance (2) within 24 h of observation. The rectangle marks the high tide period when the alga is submerged

In **variants 2–4**, polyphenol concentrations in *F. vesiculosus* and *A. nodosum* were measured for 12 h in different phases of a tidal cycle (high tide – low tide – high tide, and low tide – high tide – low tide). In the case of *F. vesiculosus*, we also analyzed the sample that was pre-acclimated in a laboratory to reveal endogenous rhythms under constant conditions.

Meteorological conditions in variants 2 and 3 (*F. vesiculosus*) differed a little. Thus, light level on 6 July (variant 2) was 60–500 mmol·m^{-2}·s^{-1}. Environmental temperature was +8.2…+9.0 °C. It was mostly cloudy, with some drizzle and fog in the afternoon. Conditions on 13 July (variant 3) featured the greatest variability. Light level was 100–1,800 mmol·m^{-2}·s^{-1}. Temperature also varied quite significantly: from +17.1 °C during the day to +9.8 °C in the evening. It was partly cloudy throughout the day. During *A. nodosum* sampling, conditions were as follows: the weather was sunny; light level was 300–1,700 mmol·m^{-2}·s^{-1}; and temperature was +13.1…+22.5 °C.

Analysis of fluctuations in polyphenol concentration in the first half-day experiment (variant 2) revealed a rise in values for the alga while its environmental conditions shifted from water to air (a peak in 11:00). Then, there was a twofold decrease in metabolite content: from 16.59 to 7.71 mg·g^{-1} dry weight, when the alga dried out. During re-submersion, concentration of polyphenols became equal to values recorded for the morning (9:00) (Fig. 2A).

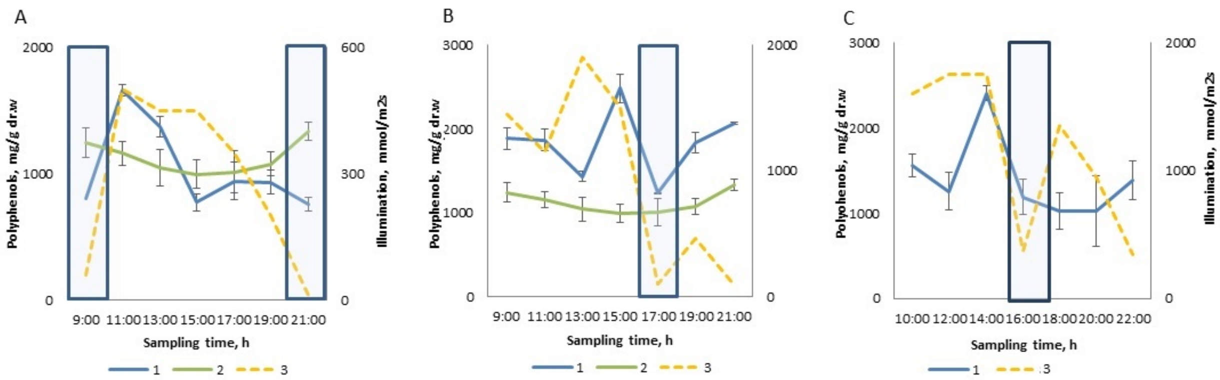

Fig. 2. Dynamics of polyphenol accumulation in algal cells within 12 h of observation: A, *Fucus vesiculosus* (variant 2, 06.07.2023); B, *F. vesiculosus* (variant 3, 13.07.2023); C, *Ascophyllum nodosum* (variant 4, 12.07.2023). 1, polyphenol accumulation in the algae under natural conditions; 2, polyphenol accumulation in the algae in a laboratory; 3, dynamics of illuminance. The rectangle marks the high tide period when the alga is submerged

In the second half-day experiment (variant 3, low tide – high tide – low tide) (Fig. 2B), one peak polyphenol content was observed: during low tide (15:00). Such an increase occurred after a considerable rise in light level. By the time of high tide (17:00), the value decreased to 11.68 mg·g^{-1} dry weight.

For comparison, polyphenol accumulation was studied in related species, *A. nodosum*, inhabiting the same littoral zone (variant 4) (Fig. 2C). One peak concentration was recorded during the observation period; it occurred in the daytime and when the alga dried out. By the time of high tide, a drop in polyphenol content to 11.90 mg·g^{-1} dry weight was noted (Fig. 2C). While the algae were submerged, metabolite concentration remained almost unchanged both in *F. vesiculosus* and *A. nodosum*; the values were in a range of 10.00–12.00 mg·g^{-1} dry weight.

Under laboratory conditions, polyphenol content in cells did not change during the entire observation period (Fig. 2A, B). The mean concentration in the submerged algae was 11.23 mg·g^{-1} dry weight (minimum we registered was 9.93 mg·g^{-1} dry weight, and maximum we recorded was 13.34).

As revealed, concentration of polyphenols is affected by such factors, as temperature and light level. Thus, the maximum accumulation was observed in the period of their highest values within a day. Within the 24-h experiment on *F. vesiculosus*, strong correlations ($p > 0.025$) were noted during day and night for both factors (Table 1).

Table 1. Spearman's correlation analysis of relationships between various environmental factors and the content of phenolic compounds in *Fucus vesiculosus* and *Ascophyllum nodosum*

Conditions	Factor		
	Environmental temperature	Light level	Tidal cycle
F. vesiculosus (24 h, variant 1)	0.7**	0.66**	–0.42
F. vesiculosus (12 h, variant 2)	–0.51	0.72*	–0.42
F. vesiculosus (12 h, variant 3)	0.1	0.1	–0.41
A. nodosum (12 h, variant 4)	0.75*	0.41	–0.2

Note: *, $p > 0.05$; **, $p > 0.025$ (statistically significant values).

For variant 2, analysis of 12-h measurements revealed a moderate inverse correlation between polyphenol content and temperature and a strong inverse correlation between the concentration of phenolic compounds and light level. For variant 3, no correlations were found.

The results obtained may be mediated by different weather conditions. During 24-h measurements, a consistent increase was recorded both in temperature and light level. Weather conditions in variant 2 were characterized by practically stable environmental temperature, and *F. vesiculosus* was chiefly affected by fluctuations in light level. For *A. nodosum*, an opposite pattern was noted: light level changed to a lesser extent than temperature. The lack of correlation in measurements in variant 3 can be explained by the fact that it was partly cloudy throughout the day of sampling: this complicated the detection of a correlation between polyphenol dynamics and environmental factors. Apparently, metabolite content depended on a complex of factors (their combination and the strength of the effect of each one).

DISCUSSION

Research conducted *in vivo* revealed significant diurnal fluctuations in polyphenol content in two species of brown algae, *F. vesiculosus* and *A. nodosum*, during the polar day on the Barents Sea coast.

For both species, it was shown *in situ* that the key changes in the concentration of polyphenols occurred in the daytime during low tide. During high tide, regardless of the time of its onset, the content of phenolic compounds remained at one level, and when algae became submerged, the value dropped.

As found for *F. vesiculosus* when investigating it *in vitro*, polyphenol concentration almost did not change throughout the day.

In macrophytes, physiological and biochemical processes are regulated by different types of endogenous rhythms and/or occur under the effect of environmental factors.

Endogenous rhythms are triggered by internal factors and adjusted when habitat conditions change, when reactive oxygen species act as the main biochemical regulators. These joint processes ensure the formation of protective reactions in an organism [Karapetyan, Dong, 2018]. Notably, some processes, such as changes in enzyme activity, as well as cell division and growth, have endogenous regulation, while other functions depend more on variations in the effect of environmental factors.

As shown in this survey, the synthesis of polyphenols is governed to a greater extent by the effect of changes in environmental factors than by endogenous rhythms. Under stable conditions (constant temperature and light level, and also absence of a drying phase), the content of metabolites remains virtually unchanged.

It was not possible to identify an unambiguous effect of environmental factors, as it was clear in one variants and not detected in others (see Table 1). Apparently, polyphenol content is affected by a combination of environmental factors: temperature, light level, and a phase of a tidal cycle.

One of the drivers of polyphenol dynamics in cells of macrophytes may be the alternation of periods when plants are submerged and dry out. The importance of this factor under natural conditions is confirmed by the detection of diurnal changes in polyphenol concentration: the dynamics coincides more with tidal processes than with changes in photoperiod. Laboratory research also showed that in the absence of drying, there are practically no variations in the content of phenolic compounds.

As reported earlier, polyphenol concentration in *F. vesiculosus* decreases when the alga is kept in water for a long time without drying [Makarov et al., 2013]. Was is also shown that occasionally drying macrophytes have higher polyphenol content than those that are constantly submerged [Pavia, Brock, 2000].

Throughout the day, factors change dynamically. Therefore, a "signal group of substances" must be formed for algae: it will trigger adaptive adjustments, so that processes of basic metabolism (protein synthesis, cell division, *etc.*) will be at the required level for a certain period.

Polyphenols perform several functions, including antioxidant ones, and are probably involved in triggering the restructuring processes in an alga when its habitat conditions change.

Daily dynamics of polyphenols is reported for different macrophytic species. Researchers analyzed some algal species inhabiting southern areas and preferring various heights of a littoral zone [Abdala-Díaz et al., 2006; Connan et al., 2007]. As shown for them, in particular for *A. nodosum*, polyphenol concentration varied within 24 h. In the daytime and during low tide, the content of metabolites was higher; however, surveys revealed no clear and express peak, as it was in our study.

Discrepancies in results obtained by us and French colleagues [Connan et al., 2007] can be explained by several reasons: we sampled different thalli fragments (apex *vs.* middle fragment); we carried out investigations in different seasons (July *vs.* March); and we dealt with different combinations of environmental factors (temperature, light level, *etc.*).

As reported in previous studies, apex and middle fragment of a thallus differ in physiological maturity and speed of response to changes in environmental factors. We used apexes, as these physiologically younger fragments are more sensitive to diurnal changes in environmental factors. Polyphenols are mostly accumulated in thallus fragments that are less strong (in particular, in apexes) and more likely to be damaged by herbivores [Mannino et al., 2014]. Polyphenols will perform a protective function, and cells will use them to repair damaged fragments [Ryzhik, Fisak, 2018].

As exemplified by measuring metabolic activity, the nature of daily changes depended on the season [Ryzhik, 2016]. The dependence of diurnal polyphenol dynamics on the season was also reported when investigating *Ericaria selaginoides* (Linnaeus) Molinari & Guiry [in paper, syn. *Cystoseira tamariscifolia* (Hudson) Papenfuss] [Abdala-Díaz et al., 2006]. The authors highlighted that larger fluctuations in parameters are typical for summer months. The analysis of the ratio of daily dynamics of polyphenols in Fucales from the Barents Sea was carried out only in summer, since this season is associated with the highest physiological activity of brown algae.

Notably, the survey on the annual dynamics of metabolite content in algae from the Murmansk coast revealed a greater dependence on the season. This could be related to the antioxidant activity of polyphenols [Ryzhik, Fisak, 2018] and the effect of temperature and light level on their synthesis.

Polyphenol concentration in *F. vesiculosus* from the Barents Sea changes during a year. Thus, the minimum is characteristic for winter and summer, while the maximum is typical for spring and autumn.

In spring, on the Murmansk coast, levels of light and UV radiation are high, an increase in duration of daylight hours is rapid as the polar night ends, and a rise in temperature is notable. Such light conditions can cause an oxidative stress, but a boost in polyphenol content allows maintaining high intensity of antioxidant processes in algal cells [Connan et al., 2006, 2007; Gómez, Huovinen, 2010]. In summer, the concentration of soluble polyphenols declines, and this may be due to slowing down growth processes and switching metabolism from growth to accumulation of reserve nutrients. Assumably, polyphenols are used as alternative nitrogen sources: correlations were found between the content of N in the environment and the concentration of tannins in cells [Ilvessalo, Tuomi, 1989; Pavia, Toth, 2000]. In autumn, polyphenol content increases again. This may result from accumulation of reserve nutrients while plants prepare for the polar night. In autumn, *F. vesiculosus* reproductive organs are formed, and polyphenols accumulated during this season can be used for formation of cell walls. Moreover, weather conditions change in autumn, and storms become frequent; those damage algae in a littoral zone and tear them off. With the onset of winter, the overall physiological activity of plants decreases. Also, the concentration of soluble polyphenols drops: metabolites that seem to be used as reserve substances to form cell walls and maintain their integrity.

For *A. nodosum* of the Barents Sea, the maximum of metabolites was observed in October [Tkach, Obluchinskaya, 2017]. For *F. vesiculosus* of the Baltic Sea, a decline in their content was noted in spring and summer, and a rise was recorded in winter [Rönnberg, Ruokolahti, 1986]. For the algae of the Northern Sea, the maximum accumulation was registered in July [Parys et al., 2009]. For several *Sargassum* species of the Sea of Japan, an increase in polyphenol content was observed in summer, a drop in winter, and an accumulation by April [Kamiya et al., 2010]. The reasons for such discrepancies may be rooted in both peculiarities of plant life cycle and the effect of a complex of abiotic factors typical for algae habitats.

In general, in all the papers we analyzed, a dependence from photoperiod was revealed, from the alternation of periods when algae are submerged and dry out, or from both parameters [Connan et al., 2007]. However, this correlation was mostly species-specific, and it was determined by the littoral horizon on which an alga grew and the effect of factors *in situ*. For *E. selaginoides* (syn. *C. tamariscifolia*), a negative correlation between diurnal polyphenol dynamics and light level was established in summer [Abdala-Díaz et al., 2006].

As already noted, polyphenols perform a variety of functions. Their participation in processes of algal development, photosynthesis, and respiration is reported, as well as in protection from UV radiation and phytopathogens, exposure to low and high temperatures, water scarcity, increased salinity, *etc.* [Abdala-Díaz et al., 2006]. Assumably, in upper-littoral plants [*Pelvetia canaliculata* (Linnaeus) Decaisne et Thuret and *A. nodosum*], cells are protected from excess UV radiation due to polyphenol accumulation during the daytime [Abdala-Díaz et al., 2006]. The same was observed in *F. vesiculosus* from the Barents Sea.

The accumulation of metabolites during the daytime can be considered as one of the mechanisms of algal adaptation and protection from oxidative processes, since polyphenols are components of the antioxidant system. In this case, the accumulation of oxidation products will trigger the synthesis or enhance the work of antioxidant enzymes, and also activate its non-enzymatic components. As assumed in several papers, changes in polyphenol concentration occur not due to their *de novo* synthesis, but due to activation of phenol sulfatase and transfer of cell-wall polyphenols to a soluble state in the cytoplasm [Abdala-Díaz et al., 2006].

Eulittoral and tidal algae [*Fucus spiralis* Linnaeus, *F. vesiculosus*, and *A. nodosum*], that grew under conditions of high light level, had a higher polyphenol content than algae of low-tidal or sublittoral zone [*Fucus serratus* Linnaeus, *Bifurcaria bifurcata* R. Ross, *Himanthalia elongata* (Linnaeus) S. F. Gray, and *Laminaria digitata* (Hudson) J. V. Lamouroux] [Abdala-Díaz et al., 2006; Connan et al., 2007; Pavia, Brock, 2000]. This data is consistent with the results of our study, and in general, it allows suggesting that daily fluctuations of phenolic compounds in *F. vesiculosus* and *A. nodosum* tissues are regulated by light level and temperature *in situ*.

In the present paper, polyphenols were measured during the polar day, when there is constant light. However, its level decreases at night. Light level can differ by tens of times during the daytime and at night. We assume that the accumulation of polyphenols and the decrease in their concentration are mainly driven by a combination of light level, temperature, and period of drying or submersion. The dynamics in polyphenol content will depend on the factor that is subjected to change to a greater extent. At a sufficiently stable environmental temperature, as in our study (an almost constant value of +8…+9 °C during the observation period under natural conditions) (the first half-day experiment), and with pronounced fluctuations in light level, the latter one was crucial. With significant fluctuations in both factors (for example, on 13.07.2023), they act together. Accordingly, it becomes difficult to determine the strength of the effect of each factor, and this is reflected in the absence of correlation. Furthermore, it was not possible to reveal the presence of daily endogenous rhythms: when environmental conditions were stable, polyphenol concentration in the algae almost did not change. This suggests that the regulation of polyphenol content occurs chiefly due to a combination of environmental factors – temperature, light level, and period of drying or submersion – and a shift in the strength of their effect.

Conclusions:

1. Polyphenol content in cells of brown algae *Fucus vesiculosus* and *Ascophyllum nodosum* sampled in the Barents Sea features pronounced daily dynamics, which depends more from environmental factors than from daily endogenous rhythms.
2. In summer (the polar day), the diurnal dynamics in concentration of polyphenols is characterized by one express peak in the daytime.
3. The key factors affecting polyphenol content are light level, temperature, and alternation of algal drying and submersion. When the algae are submerged, polyphenol concentration decreases.

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REFERENCES

1. Bogolitsyn K. G., Druzhinina A. S., Ovchinnikov D. V., Kaplitsin P. A., Shulgin E. V., Parshina A. E. Polyphenols of brown algae. *Khimiya rastitel'nogo syr'ya*, 2018, no. 3, pp. 5–21. (in Russ.). https://doi.org/10.14258/jcprm.2018031898
2. *Rasteniya i lishainiki murmanskogo poberezh'ya Barentseva morya* : field atlas. Petrozavodsk : Izd-vo PetrGU, 2016, 191 p. (in Russ.)
3. Ryzhik I. V., Fisak E. M. The annual dynamics of the content of soluble phlorotannins in the cells of *Fucus vesiculosus* L. and their possible role in the repair processes of damaged tissue. *Voprosy sovremennoi al'gologii*, 2018, no. 1 (16). (in Russ.). URL: http://algology.ru/1248 [accessed: 29.09.2024].
4. Tkach A. V., Obluchinskaya E. D. Sterols and polyphenols of fucoids from the Murmansk coast of the Barents Sea. *Vestnik MGTU. Trudy Murmanskogo gosudarstvennogo tekhnicheskogo universiteta*, 2017, vol. 20, no. 2, pp. 326–335. (in Russ.). https://elibrary.ru/zchvlx
5. Abdala-Díaz R. T., Cabello-Pasini A., Pérez-Rodríguez E., Conde Álvarez R. M., Figueroa F. L. Daily and seasonal variations of optimum quantum yield and phenolic compounds in *Cystoseira tamariscifolia* (Phaeophyta). *Marine Biology*, 2006, vol. 148, iss. 3, pp. 459–465. https://doi.org/10.1007/s00227-005-0102-6
6. Aminina N. M., Vishnevskaya T. I., Karaulova E. P., Epur N. V., Yakush E. V. Prospects for the use of commercial and potentially commercial brown algae of the Far Eastern seas as a source of polyphenols. *Russian Journal of Marine Biology*, 2020, vol. 46, iss. 1, pp. 34–41. https://doi.org/10.1134/s1063074020010022
7. Arnold T. M., Targett N. M. Evidence for metabolic turnover of polyphenolics in tropical brown algae. *Journal of Chemical Ecology*, 2000, vol. 26, iss. 6, pp. 1393–1410. https://doi.org/10.1023/a:1005588023887
8. Arnold T. M., Targett N. M. Quantifying *in situ* rates of phlorotannin synthesis and polymerization in marine brown algae. *Journal of Chemical Ecology*, 1998, vol. 24, iss. 3, pp. 577–595. https://doi.org/10.1023/a:1022373121596
9. Connan S. *Etude de la diversité spécifique des macroalgues de la Pointe de Bretagne et analyse des composés phénoliques des Phéophycées dominantes.* PhD thesis. Brest, 2004.
10. Connan S., Delisle F., Deslandes E., Ar Gall E. Intra-thallus phlorotannin content and antioxidant activity in Phaeophyceae of temperate waters. *Botanica Marina*, 2006, vol. 49, iss. 1, pp. 39–46. https://doi.org/10.1515/bot.2006.005
11. Connan E., Deslandes E., Ar Gall E. Influence of day–night and tidal cycles on phenol content and antioxidant capacity in three temperate intertidal brown seaweeds. *Journal of Experimental Marine Biology and Ecology*, 2007, vol. 349, iss. 2, pp. 360–365. https://doi.org/10.1016/j.jembe.2007.05.028
12. Connan S., Goulard F., Stiger V., Deslandes E., Ar Gall E. Interspecific and temporal variation in phlorotannin levels in an assemblage of brown algae. *Botanica Marina*, 2004, vol. 47, iss. 5, pp. 410–416. https://doi.org/10.1515/bot.2004.057
13. Dubois A., Iken K. Seasonal variation in kelp phlorotannins in relation to grazer abundance and environmental variables in the Alaskan sublittoral zone. *Algae*, 2012, vol. 27, no. 1, pp. 9–19. https://doi.org/10.4490/algae.2012.27.1.009

14. Gómez I., Huovinen P. Induction of phlorotannins during UV exposure mitigates inhibition of photosynthesis and DNA damage in the kelp *Lessonia nigrescens*. *Photochemistry and Photobiology*, 2010, vol. 86, iss. 5, pp. 1056–1063. https://doi.org/10.1111/j.1751-1097.2010.00786.x
15. Ilvessalo H., Tuomi J. Nutrient availability and accumulation of phenolic compounds in the brown alga *Fucus vesiculosus*. *Marine Biology*, 1989, vol. 101, iss. 1, pp. 115–119. https://doi.org/10.1007/bf00393484
16. Jennings J. G., Steinberg P. D. Phlorotannins *versus* other factors affecting epiphyte abundance on the kelp *Ecklonia radiata*. *Oecologia*, 1997, vol. 109, iss. 3, pp. 461–473. https://doi.org/10.1007/s004420050106
17. Jormalainen V., Honkanen T., Koivikko R., Eränen J. Induction of phlorotannin production in a brown alga: Defense or resource dynamics? *Oikos*, 2003, vol. 103, no. 3, pp. 640–650. https://doi.org/10.1034/j.1600-0706.2003.12635.x
18. Kamiya M., Nishio T., Yokoyama A., Yatsuya K., Nishigaki T., Shinya Y., Ohki K. Seasonal variation of phlorotannin in sargassacean species from the coast of the Sea of Japan. *Phycological Research*, 2010, vol. 58, iss. 1, pp. 53–61. https://doi.org/10.1111/j.1440-1835.2009.00558.x
19. Karapetyan S., Dong X. Redox and the circadian clock in plant immunity: A balancing act. *Free Radical Biology and Medicine*, 2018, vol. 119, pp. 56–61. https://doi.org/10.1016/j.freeradbiomed.2017.12.024
20. Klindukh M. P., Ryzhik I. V., Makarov M. V. Influence of environmental factors on the contents of free amino acids in *Fucus vesiculosus* in the Barents Sea during the day. *E3S Web of Conferences*, 2023, vol. 390, iss. 2, art. 05008 (6 p.). https://doi.org/10.1051/e3sconf/202339005008
21. Koivikko R., Loponen J., Honkanen T., Jormalainen V. Contents of soluble, cell-wall-bound and exuded phlorotannins in the brown alga *Fucus vesiculosus*, with implications on their ecological functions. *Journal of Chemical Ecology*, 2005, vol. 31, iss. 1, pp. 195–212. https://doi.org/10.1007/s10886-005-0984-2
22. Makarov M. V., Ryzhik I. V., Voskoboinikov G. M. The effect of *Fucus vesiculosus* L. (Phaeophyceae) depth of vegetation in the Barents Sea (Russia) on its morphophysiological parameters. *International Journal on Algae*, 2013, vol. 15, iss. 1, pp. 77–90. https://doi.org/10.1615/interjalgae.v15.i1.60
23. Mannino A. M., Vaglica V., Oddo E. Seasonal variation in total phenolic content of *Dictyopteris polypodioides* (Dictyotaceae) and *Cystoseira amentacea* (Sargassaceae) from the Sicilian coast. *Flora Mediterranea*, 2014, vol. 24, pp. 39–50. https://doi.org/10.7320/flmedit24.039
24. Mezghani S., Dezső C., Bourguiba I., Hohmann J., Mohamed A., Bouaziz M. Characterization of phenolic compounds of *Ulva rigida* (Chlorophycae) and its antioxidant activity. *European Journal of Medicinal Plants*, 2016, vol. 12, iss. 1, art. ejmp.22935 (9 p.). https://doi.org/10.9734/ejmp/2016/22935
25. Parys S., Kehraus S., Pete R., Küpper F. C., Glombitza K.-W., König G. M. Seasonal variation of polyphenolics in *Ascophyllum nodosum* (Phaeophyceae). *European Journal of Phycology*, 2009, vol. 44, iss. 3, pp. 331–338. https://doi.org/10.1080/09670260802578542
26. Pavia H., Brock E. Extrinsic factors influencing phlorotannin production in the brown alga *Ascophyllum nodosum*. *Marine Ecology Progress Series*, 2000, vol. 193, pp. 285–294. https://doi.org/10.3354/meps193285
27. Pavia H., Cervin G., Lindgren A., Åberg P. Effects of UV-B radiation and simulated herbivory on phlorotannins in the brown alga *Ascophyllum nodosum*. *Marine Ecology*

Progress Series, 1997, vol. 157, pp. 139–146. https://doi.org/10.3354/meps157139

28. Pavia H., Toth G. B. Influence of light and nitrogen on the phlorotannin content of the brown seaweeds *Ascophyllum nodosum* and *Fucus vesiculosus*. *Hydrobiologia*, 2000, vol. 440, iss. 1–3, pp. 299–305. https://doi.org/10.1023/a:1004152001370
29. Peckol P., Krane J. M., Yates J. L. Interactive effects of inducible defense and resource availability on phlorotannins in the North Atlantic brown alga *Fucus vesiculosus*. *Marine Ecology Progress Series*, 1996, vol. 138, pp. 209–217. https://doi.org/10.3354/meps138209
30. Pedersen A. Studies on phenol content and heavy metal uptake in fucoids. *Hydrobiologia*, 1984, vol. 116, iss. 1–3, pp. 498–504. https://doi.org/10.1007/bf00027732
31. Ragan M. A., Jensen A. Quantitative studies on brown algal phenols. II. Seasonal variation in polyphenol content of *Ascophyllum nodosum* (L.) Le Jol. and *Fucus vesiculosus* (L.). *Journal of Experimental Marine Biology and Ecology*, 1978, vol. 34, iss. 3, pp. 245–258. https://doi.org/10.1016/s0022-0981(78)80006-9
32. Ragan M. A., Glombitza K. W. Phlorotannins, brown algal polyphenols. In: *Progress in Phycological Research* / F. E. Round, D. J. Chapman (Eds). Bristol, UK : Biopress, 1986, vol. 4, pp. 129–241.
33. Reboleira J., Silva S., Chatzifragkou A., Niranjan K., Lemos M. F. L. Seaweed fermentation within the fields of food and natural products. *Trends in Food Science & Technology*, 2021, vol. 116, pp. 1056–1073. https://doi.org/10.1016/j.tifs.2021.08.018
34. Rönnberg O., Ruokolahti C. Seasonal variation of algal epiphytes and phenolic content of *Fucus vesiculosus* in a northern Baltic archipelago. *Annales Botanici Fennici*, 1986, vol. 23, no. 4, pp. 317–323.
35. Ryzhik I. V. Seasonal variations in the metabolic activity of cells of *Fucus vesiculosus* Linnaeus, 1753 (Phaeophyta: Fucales) from the Barents Sea. *Russian Journal of Marine Biology*, 2016, vol. 42, iss. 5, pp. 433–436. https://doi.org/10.1134/s1063074016050102
36. Schoenwaelder M. E. A. The occurrence and cellular significance of physodes in brown algae. *Phycologia*, 2002, vol. 41, iss. 2, pp. 125–139. https://doi.org/10.2216/i0031-8884-41-2-125.1
37. Schoenwaelder M. E. A., Clayton M. N. The presence of phenolic compounds in isolated cell walls of brown algae. *Phycologia*, 1999, vol. 38, iss. 3, pp. 161–166. https://doi.org/10.2216/i0031-8884-38-3-161.1
38. Steinberg P. D. Effects of quantitative and qualitative variation in phenolic compounds on feeding in three species of marine invertebrate herbivores. *Journal of Experimental Marine Biology and Ecology*, 1988, vol. 120, iss. 3, pp. 221–237. https://doi.org/10.1016/0022-0981(88)90003-2
39. Steinberg P. D. Seasonal variation in the relationship between growth rate and phlorotannin production in the kelp *Ecklonia radiata*. *Oecologia*, 1995, vol. 102, iss. 2, pp. 169–173. https://doi.org/10.1007/bf00333248
40. Van Alstyne K. L., McCarthy III J. J., Hustead C. L., Duggins D. O. Geographic variation in polyphenolic levels of Northeastern Pacific kelps and rockweeds. *Marine Biology*, 1999, vol. 133, iss. 2, pp. 371–379. https://doi.org/10.1007/s002270050476
41. Van Alstyne K. L., Whitman S. L., Ehlig J. M. Differences in herbivore preferences, phlorotannin production, and nutritional quality between juvenile and adult tissues from marine brown algae. *Marine Biology*, 2001, vol. 139, iss. 1, pp. 201–210. https://doi.org/10.1007/s002270000507

СУТОЧНАЯ ДИНАМИКА НАКОПЛЕНИЯ ПОЛИФЕНОЛОВ В КЛЕТКАХ *FUCUS VESICULOSUS* L. И *ASCOPHYLLUM NODOSUM* (L.) LE JOLIS В ПЕРИОД ПОЛЯРНОГО ДНЯ НА ПОБЕРЕЖЬЕ БАРЕНЦЕВА МОРЯ

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Полифенолы — группа вторичных метаболитов, которые защищают организм от ультрафиолетового излучения, участвуют в метаболизме растения, а также обладают терапевтическими свойствами. Изучение динамики накопления полифенолов в бурых водорослях (Phaeophyceae: Fucales) представляет значительный интерес для понимания механизмов адаптации этих организмов к изменяющимся условиям среды. Цель работы — выявить суточные изменения содержания полифенолов в *Fucus vesiculosus* Linnaeus и *Ascophyllum nodosum* (Linnaeus) Le Jolis, произрастающих на побережье Баренцева моря, проанализировать зависимость их накопления от освещённости и температуры, а также определить роль эндогенных ритмов и внешних факторов в регуляции метаболизма полифенолов в клетках. Исследование проведено в июле 2022 и 2023 гг. на побережье Баренцева моря (как в естественной среде, так и в лабораторных условиях). Для анализа содержания полифенолов применён спектрофотометрический метод Фолина — Чокалтеу. Показана значительная суточная динамика полифенолов. Основные изменения содержания веществ происходят в естественных условиях — в дневное время и в период отлива, при осушении талломов. Во время прилива, когда талломы находятся в погружённом состоянии, концентрация полифенолов не изменяется. Содержание полифенолов зависит от сочетанного воздействия уровня освещённости, температуры и чередования периодов погружения и осушения. В лабораторных условиях суточный ритм изменения концентрации полифенолов не сохраняется, что может свидетельствовать о сниженной роли эндогенных ритмов и о главенствующей роли факторов внешней среды в регуляции синтеза полифенолов. Полученные данные расширяют знания о физиолого-биохимических особенностях фукусовых водорослей арктической зоны, а также о механизмах адаптации растений к произрастанию в приливно-отливной зоне морей. Результаты исследования можно использовать при разработке технологии аквакультуры водорослей для получения сырья с заданными свойствами.

Ключевые слова: полифенолы, Fucales, температура, освещённость, приливно-отливный цикл, полярный день, Баренцево море