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DYNAMICS OF FREE AMINO ACIDS IN THE BROWN ALGA *FUCUS VESICULOSUS* LINNAEUS, 1753 FROM THE BARENTS SEA THROUGHOUT THE YEAR

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Free amino acids (FAA) are a significant biochemical component of any cell. Their composition and content depend on physiological state, abiotic environmental factors, and a developmental phase of the organism. Their functions in plants are very diverse; those include participation in both the synthesis of proteins and other compounds and the adaptation to adverse environmental conditions. Information on the FAA dynamics is of key importance for understanding their role in formation of algae resistance to varying environmental factors. The aim of this study is to determine the FAA content in the brown alga *Fucus vesiculosus* and its seasonal changes, as well as to reveal the dependence on environmental factors and the alga developmental phase. The alga for research was sampled in the Kola Bay littoral (the Barents Sea) during low tide once a month from December 2015 to December 2016. The middle part of the thallus was used for the study. The FAA qualitative and quantitative composition was determined by high-performance liquid chromatography. The FAA qualitative composition did not change throughout the year; in the FAA pool, glutamic and aspartic acids, alanine, and proline prevailed. The FAA content varied throughout the year; the maximum amount was recorded in spring–summer. The FAA content depended on external environmental factors. The correlations were determined between the content of individual FAA and air temperature, water temperature, and salinity. The FAA dynamics in different developmental phases of *F. vesiculosus* was associated with processes occurring in the alga; it is affected by growth rate, cell metabolic activity, photosynthesis rate, and generative development. Each phase was characterized by its own dynamics of the FAA content. Based on the dynamics of the FAA concentration in *F. vesiculosus*, correspondences were found with the developmental phases – dormancy, growth activation, growth, and storage. Free glutamate and aspartate may act as one of the reserve sources of organic nitrogen in this alga. Apparently, the transport of organic forms of nitrogen in *F. vesiculosus* thallus is carried out by glutamate, aspartate, alanine, and proline.

Keywords: *Fucus vesiculosus*, free amino acids, seasonal changes, developmental phases, temperature, salinity, Barents Sea

Amino acids are biochemical compounds necessary for the life of any organism. In the organism, those are in two states – bound and free. Free amino acids (hereinafter FAA) are involved in the construction of protein and peptide molecules, as well as in the synthesis of nitrogenous and nitrogen-free compounds – nucleotides, phytohormones, vitamins, alkaloids, betaines, pigments, polyphenols, *etc.* (Hildebrandt et al., 2015 ; Parthasarathy et al., 2018 ; Rhodes & Hanson, 1993 ; Zrenner et al., 2006). Moreover, FAA act as signaling molecules (Lam et al., 1998 ; Oliveira & Coruzzi, 1999), are involved in plant adaptation to varying environmental conditions (Galili & Höfgen, 2002 ; Stewart & Larher, 1980), and serve as antioxidants, osmoregulators, and cryoprotectants (Harris & Logan, 2018 ; Jackson & Seppelt, 1995 ;

Stewart & Larher, 1980 ; Trovato et al., 2008). In algae, as well as in higher plants, FAA participate in the transport of organic nitrogen along the thallus; those can act as reserve sources of nitrogen and be accumulated for further use in growth and development during a period of its low content in the environment (Diouris, 1989 ; Naldi & Wheeler, 1999 ; Schmitz & Srivastava, 1979). FAA are involved in many metabolic processes in plants and indicate the physiological state of an organism.

Fucus vesiculosus Linnaeus, 1753 is one of the most common algal species in the Barents Sea. Recently, much attention has been paid to the study of its physiological peculiarities as a model object for investigating mechanisms of algal adaptation to high latitude conditions (Makarov et al., 2010 ; Ryzhik, 2016 ; Ryzhik et al., 2021 ; Tropin et al., 2003). However, data on the FAA content are scarce and mainly obtained by single or duplicate algal sampling aimed at determining the possibility of their use as raw material for various process industries (Repina, 2005 ; Klindukh & Obluchinskaya, 2018 ; Maehre et al., 2014 ; Mouritsen et al., 2019 ; Peinado et al., 2014). At the same time, changes in the FAA composition and content depending on external environmental factors and the plant developmental phase are almost not described. Moreover, there is a lack of material on FAA significance and role for algae themselves. These data are of key importance for understanding the FAA participation in formation of adaptation and in maintaining organism stability in varying environmental conditions.

The aim of the work is to determine the FAA content in the brown alga *F. vesiculosus* and to reveal its seasonal changes and dependence on environmental factors and the alga developmental phase.

MATERIAL AND METHODS

To study the seasonal dynamics of the FAA composition and content in the brown alga *F. vesiculosus*, the material was sampled monthly from December 2015 to December 2016 in the Kola Bay littoral (the Barents Sea) during low tide (the Abram-Mys area; 68°58′N, 33°01′E). Alga samples were fertile, with 7–10 dichotomous branches. Simultaneously, water and air temperatures were measured with a mercury thermometer (TL-4, Russia), and water salinity was measured with a salinity refractometer (RHS-10ATC, China). For the study, the middle part of the thallus was used (the 4^{th} and 5^{th} dichotomous branches) – as the most mature and active part. In the alga (5–6 thalli), a part of the thallus was separated, cut, and fixed with 96 % ethanol. Fixed samples were stored in a dark and cool place in sealed test tubes.

FAA were extracted from the samples with 70 % ethanol heated up to +60…+70 °C: the alcohol extract was poured off, and the alga was grinded in a mortar with glass sand and then poured with 7 mL of hot 70 % ethanol. The alga was infused with constant stirring for 1 h, and the mixture was centrifuged for 5 min at 3,000 rpm to separate the precipitate. The extract was poured into an evaporating cup, and the precipitate was refilled with hot ethanol. The extraction process was repeated 3 times. The resulting extracts were combined and evaporated to dryness on a water bath. The precipitate was dissolved in 10 mL of distilled water and centrifuged for 10 min at 5,000 rpm; the purification was carried out by ion-exchange chromatography on a KU-2-8 cation exchanger (Metody, 1975). The dry precipitate obtained after purification was dissolved in a small amount of distilled water and used to determine FAA.

The FAA composition and content were analyzed according to the standard method on a Shimadzu LC-20AD Prominence liquid chromatograph (Japan) with a Shimadzu SPD-M20A Prominence photodiode array detector and 250 × 4.6 mm Supelco C18 chromatographic column, 5 μm (the USA) (Rudenko et al., 2010). The measurement was carried out in two parallel samples in duplicate (n = 4). Data on the FAA content are presented as “mean value ± standard deviation.”

The dry matter content in the samples was determined in duplicate according to the standard method: an algal sample with a raw weight of about 1 g was dried to a constant weight for a day at a temperature of +100…+105 °C (GOST 26185-84, 2004).

Using the one-way analysis of variance (ANOVA), the effects of the season, air temperature, water temperature, and water salinity on the FAA content in the alga were determined. Applying the Pearson correlation coefficient, the relationship between the FAA content and salinity, air temperature, and water temperature was identified. To establish significant differences in the FAA content in the alga in different seasons of the year, the Tukey–Kramer multiple comparison test was used. The data were statistically processed at a significance level of $p \leq 0.05$. Data processing and calculations were carried out in Microsoft Excel 2010, NCSS 2004, and PAST v3.22.

RESULTS

At the *F. vesiculosus* sampling site, data on variability of environmental factors were obtained (Table 1). From spring to early autumn, water salinity did not exceed 20 ‰; the lowest values were recorded in May and June 2016. In winter months and in October, it varied within 20–30 ‰. The obtained data on the dynamics of coastal water salinity are typical for the southern bend of the Kola Bay (Kola Bay, 2009). The highest water and air temperatures were recorded in June–August in the Abram-Mys area. Minimum values of water temperature were registered in January–March, and of air temperature, in November–April.

Table 1. Values of some environmental factors during alga sampling

Month and year	Water salinity, ‰	Water temperature, °C	Air temperature, °C
December 2015	19.5	+3.1	–1.2
January 2016	30	–1.5	–30
February 2016	25	–0.6	–4.4
March 2016	18.5	–0.1	–3.8
April 2016	17	+1.3	–1.6
May 2016	7	+7.6	+15.3
June 2016	7.5	+14.2	+18.9
July 2016	12.5	+12.4	+13.8
August 2016	15	+11.1	+11.7
September 2016	17	+9.5	+10.7
October 2016	25	+4.9	+3.2
November 2016	17	+2.4	–1.6
December 2016	20	+2.3	+0.5

Throughout the year, 20 FAA were identified in *F. vesiculosus* thallus (Fig. 1, Table 2). The main part of the FAA pool was represented by aspartic acid (aspartate), glutamic acid (glutamate), alanine, and proline. The prevailing amino acid did not change throughout the year. Glutamic acid remained prevailing one in the FAA composition – 33.9–70.6 % of the total amount of FAA and, accordingly, determined the nature of the change in the total amount of FAA throughout the year. It was followed by aspartic acid, alanine, and proline. In general, the concentrations of other FAA throughout the year did not exceed 2 %. The content of methionine and hydroxyproline in the FAA pool of *F. vesiculosus* was the lowest – less than 0.009 mg·g^{-1} dry weight.

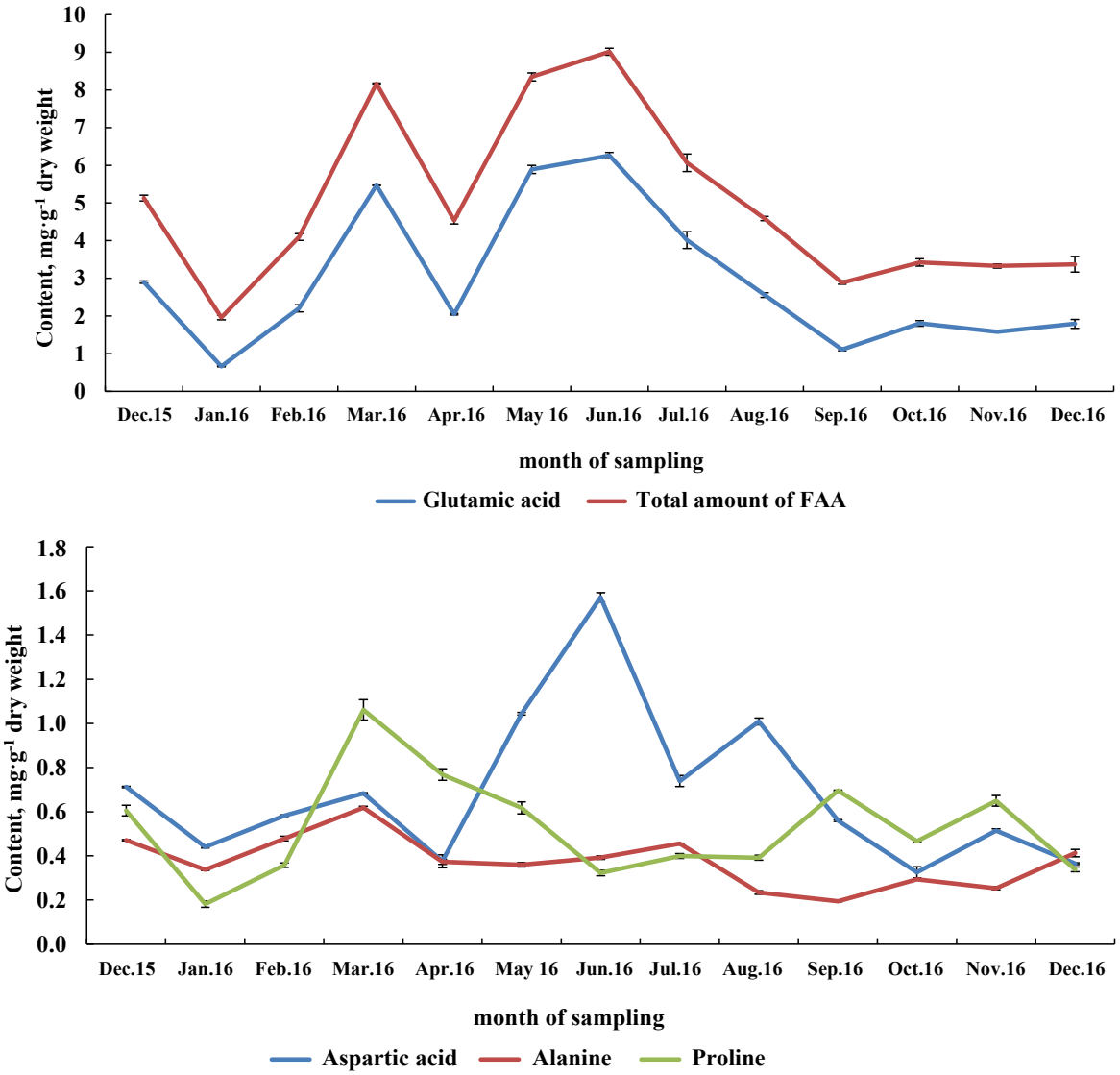

Fig. 1. Dynamics of concentration of dominant free amino acids and their sum in *Fucus vesiculosus* (mean value ± standard deviation; $n = 4$) throughout the year

The mean concentration of 12 FAA in *F. vesiculosus* varied significantly depending on the season (spring, summer, winter, and autumn). At the same time, the concentrations of valine, glycine, leucine, isoleucine, serine, tyrosine, and phenylalanine did not differ significantly between seasons, despite considerable differences in their content in each month of the year (Tables 2 and 3). In spring and/or summer, the concentrations of aspartate, hydroxyproline, histidine, glutamate, methionine, and cystine + cysteine were higher than in autumn and winter. In other FAA, the highest mean concentrations *per* season were recorded not only in spring and summer, but also in autumn or winter.

Analyzing the annual dynamics of the FAA concentration in *F. vesiculosus*, one can distinguish winter–spring, spring–summer, summer–autumn, and autumn–winter periods. In the winter–spring period (from January to March), there was a gradual rise in the FAA concentration in the alga thalli (Fig. 1). The content of all prevailing amino acids increased: glutamate, by 8.2 times; aspartate, by 1.6 times; alanine, by 1.8 times; and proline, by 5.9 times. Alanine and proline concentrations had the maximum values for the entire observation period.

Table 2. Concentration of free amino acids in *Fucus vesiculosus* (mean value ± standard deviation; $n = 4$), mg·g^{-1} dry weight

Amino acid	2015	2016											
	December	January	February	March	April	May	June	July	August	September	October	November	December
Arginine	0.027 ± 0.001	0.016 ± 0.001	0.023 ± 0.0005	0.037 ± 0.001	0.013 ± 0.001	0.040 ± 0.002	0.049 ± 0.002	0.027 ± 0.0003	0.043 ± 0.004	0.066 ± 0.001	0.030 ± 0.001	0.041 ± 0.002	0.034 ± 0.002
Valine	0.042 ± 0.0005	0.020 ± 0.0001	0.024 ± 0.0003	0.031 ± 0.001	0.034 ± 0.003	0.034 ± 0.002	0.041 ± 0.0004	0.030 ± 0.002	0.026 ± 0.001	0.022 ± 0.001	0.032 ± 0.002	0.024 ± 0.001	0.025 ± 0.002
Hydroxyproline	0.002 ± 0.0002	0.002 ± 0.0001	0.003 ± 0.0002	0.005 ± 0.001	0.007 ± 0.0001	0.009 ± 0.0004	0.007 ± 0.00004	0.002 ± 0.0001	0.005 ± 0.0003	0.003 ± 0.00004	0.003 ± 0.00004	0.005 ± 0.00005	0.004 ± 0.0001
Histidine	0.028 ± 0.002	0.033 ± 0.0004	0.052 ± 0.002	0.062 ± 0.001	0.020 ± 0.001	0.064 ± 0.002	0.077 ± 0.001	0.041 ± 0.002	0.058 ± 0.002	0.045 ± 0.002	0.011 ± 0.001	0.052 ± 0.002	0.048 ± 0.006
Glycine	0.048 ± 0.001	0.017 ± 0.001	0.023 ± 0.001	0.020 ± 0.001	0.041 ± 0.003	0.027 ± 0.002	0.033 ± 0.002	0.033 ± 0.001	0.024 ± 0.002	0.021 ± 0.0002	0.031 ± 0.003	0.021 ± 0.001	0.025 ± 0.001
Isoleucine	0.021 ± 0.001	0.009 ± 0.0001	0.008 ± 0.0001	0.008 ± 0.0003	0.013 ± 0.0003	0.010 ± 0.0005	0.012 ± 0.0004	0.012 ± 0.001	0.013 ± 0.0001	0.009 ± 0.0002	0.014 ± 0.001	0.009 ± 0.0005	0.011 ± 0.0001
Leucine	0.019 ± 0.001	0.008 ± 0.0002	0.009 ± 0.0001	0.006 ± 0.0003	0.022 ± 0.001	0.008 ± 0.0001	0.009 ± 0.0003	0.014 ± 0.0001	0.014 ± 0.002	0.006 ± 0.0003	0.020 ± 0.001	0.008 ± 0.0005	0.015 ± 0.0001
Lysine	0.023 ± 0.0003	0.015 ± 0.0001	0.011 ± 0.0003	0.006 ± 0.0002	0.007 ± 0.001	0.012 ± 0.001	0.014 ± 0.0003	0.010 ± 0.001	0.020 ± 0.001	0.005 ± 0.00001	0.019 ± 0.0001	0.008 ± 0.001	0.011 ± 0.0001
Methionine	0.002 ± 0.0002	0.002 ± 0.0002	0.003 ± 0.0005	0.001 ± 0.0002	0.004 ± 0.00004	0.003 ± 0.001	0.005 ± 0.0002	0.003 ± 0.0001	0.004 ± 0.00003	0.002 ± 0.000002	0.003 ± 0.0002	0.002 ± 0.00003	0.002 ± 0.0001
Serine	0.081 ± 0.0002	0.052 ± 0.001	0.052 ± 0.003	0.054 ± 0.002	0.056 ± 0.003	0.056 ± 0.003	0.066 ± 0.002	0.058 ± 0.0005	0.048 ± 0.001	0.048 ± 0.002	0.056 ± 0.002	0.059 ± 0.001	0.057 ± 0.002
Threonine	0.045 ± 0.001	0.022 ± 0.001	0.022 ± 0.0002	0.021 ± 0.002	0.049 ± 0.001	0.025 ± 0.002	0.039 ± 0.0003	0.043 ± 0.002	0.031 ± 0.001	0.033 ± 0.0002	0.044 ± 0.002	0.036 ± 0.001	0.026 ± 0.001
Tyrosine	0.024 ± 0.001	0.015 ± 0.0001	0.017 ± 0.0001	0.005 ± 0.0001	0.064 ± 0.003	0.008 ± 0.0003	0.009 ± 0.001	0.022 ± 0.001	0.017 ± 0.001	0.007 ± 0.0001	0.035 ± 0.0005	0.006 ± 0.0002	0.018 ± 0.003
Tryptophan	0.017 ± 0.001	0.014 ± 0.001	0.014 ± 0.001	0.013 ± 0.001	0.004 ± 0.0003	0.008 ± 0.0003	0.013 ± 0.0001	0.009 ± 0.0001	0.017 ± 0.0001	0.013 ± 0.0001	0.014 ± 0.0001	0.012 ± 0.0001	0.012 ± 0.0003
Phenylalanine	0.039 ± 0.001	0.081 ± 0.002	0.153 ± 0.003	0.024 ± 0.001	0.370 ± 0.032	0.040 ± 0.0005	0.020 ± 0.001	0.101 ± 0.009	0.036 ± 0.003	0.016 ± 0.001	0.149 ± 0.005	0.015 ± 0.001	0.124 ± 0.019
Cystine + cysteine	0.025 ± 0.002	0.031 ± 0.002	0.060 ± 0.004	0.043 ± 0.004	0.265 ± 0.015	0.090 ± 0.004	0.072 ± 0.001	0.051 ± 0.005	0.040 ± 0.002	0.032 ± 0.001	0.070 ± 0.005	0.030 ± 0.004	0.057 ± 0.010

Table 3. Mean concentration of free amino acids in different seasons and results of ANOVA of the influence of the sampling season on the FAA content ($n = 44$)

Amino acid	$F_{(3, 40)}$	p	Mean concentration *per* season, mg·g^{-1} dry weight			
			Winter	Spring	Summer	Autumn
Alanine	10.92	≤ 0.0001	0.425*	0.450*	0.361*	0.247
Arginine	7.69	0.0004	0.025	0.030	0.040*	0.046*
Aspartic acid	11.40	≤ 0.0001	0.525	0.701	1.106*	0.467
Valine	2.26	0.096	0.028	0.033	0.032	0.026
Histidine	3.40	0.027	0.040	0.049*	0.059*	0.036
Glycine	0.57	0.639	0.028	0.029	0.030	0.024
Glutamic acid	16.71	≤ 0.0001	1.889	4.468*	4.278*	1.499
Isoleucine	1.24	0.309	0.012	0.010	0.012	0.011
Leucine	0.20	0.898	0.013	0.012	0.012	0.011
Lysine	4.82	0.006	0.015*	0.008	0.015*	0.011
Methionine	9.30	≤ 0.0001	0.002	0.003	0.004*	0.002
Proline	23.61	≤ 0.0001	0.371	0.816*	0.371	0.604*
Serine	0.73	0.538	0.060	0.055	0.057	0.054
Threonine	2.95	0.040	0.029	0.032	0.038*	0.038*
Tyrosine	0.39	0.764	0.019	0.026	0.016	0.016
Tryptophan	6.49	0.001	0.014*	0.008	0.013*	0.013*
Phenylalanine	1.29	0.291	0.099	0.144	0.053	0.060
Cystine + cysteine	5.93	0.002	0.043	0.133*	0.054	0.044
Hydroxyproline	15.60	≤ 0.0001	0.003	0.007*	0.005	0.004
Total amount of FAA	19.03	≤ 0.0001	3.640	7.015*	6.556*	3.212

Note: * denotes the highest values. Differences in the mean FAA concentration for the season were determined according to the Tukey–Kramer multiple comparisons test ($n = 44$; $DF = 40$; $\alpha = 0.05$).

In the spring–summer period (from April to June), significant changes in the FAA concentration in *F. vesiculosus* were observed. In April, the content of prevailing amino acids (glutamic acid, alanine, aspartate, and proline) decreased, as well as the content of arginine, histidine, and tryptophan. The concentration of phenylalanine, threonine, cystine + cysteine, glycine, tyrosine, leucine, isoleucine, and methionine increased (Fig. 1, Table 2). In May and June, FAA were accumulated. During this period, the concentrations of glutamate and aspartate in the studied *F. vesiculosus* samples increased and reached the highest values – (6.261 ± 0.083) and (1.571 ± 0.021) mg·g^{-1} dry weight, respectively. The content of alanine and proline decreased; by June, their levels were equal to winter ones.

The summer–autumn period (from July to September) was characterized by a drop in the content of the total amount of FAA and most of individual FAA. Specifically, compared with the values in early summer, the concentrations of glutamate, aspartate, and alanine decreased by 2–5.6 times, while the content of proline, on the contrary, increased by 2.2 times.

In the autumn–winter period (from October to December), the FAA concentration in *F. vesiculosus* was low. In October, the total amount of FAA increased compared to that in September; it remained stable until December – within a range from (3.327 ± 0.056) to (3.421 ± 0.098) mg·g^{-1} dry weight. In January, the total amount of FAA in alga thalli decreased and reached its lowest values – (1.959 ± 0.061) mg·g^{-1} dry weight. The content of glutamate varied in a similar way during this period reaching the minimum values for the year – (0.664 ± 0.013) mg·g^{-1} dry weight (Fig. 1). By December, the concentration of alanine increased by 2.1 times compared to the value in September; in January, it decreased by 1.2 times. In December–January, there was a gradual decrease in the content of both aspartic acid and proline.

DISCUSSION

In *F. vesiculosus*, three developmental phases are distinguished throughout the year – the dormancy phase (autumn–winter), the growth phase (spring–early summer), and the storage phase (summer) (Kuznetsov & Schoschina, 2003 ; Ryzhik, 2016). Analyzing the nature of the FAA content changes in the middle part of *F. vesiculosus* thallus obtained in this work, it is possible to distinguish the fourth developmental phase by dividing the growth phase into two – the growth activation phase (winter–spring) and the actual growth phase (spring–summer). Other phases coincide in time with those distinguished earlier. *F. vesiculosus* developmental phases differ in the cell metabolic activity, intensity of photosynthesis, growth rate, and generative development. These alterations are aimed at performing certain processes in different seasons: in summer and autumn, at reproduction and preparation for winter; in spring, at the thallus growth; and in winter, at a rest and adaptation to adverse environmental conditions.

The **dormancy phase** of *F. vesiculosus* covers the autumn–winter period. At this time, the alga is characterized by a minimum growth rate (September–February), as well as by formation, laying, and slow development of reproductive structures (October–February) (Kuznetsov & Schoschina, 2003 ; Makarov et al., 1995). The cell metabolic activity gradually decreases in autumn and is minimal in winter. In late January and early February, physiological processes become more active, and the intensity of photosynthesis increases (Kuznetsov & Schoschina, 2003 ; Ryzhik, 2007, 2016). For the FAA content in September–January, low concentrations of glutamic acid, aspartate, and alanine are characteristic. This is due to low intensity of metabolism and photosynthesis and a lack of need for FAA as structural elements. By changes in FAA, this period can be characterized as the dormancy phase as well.

Since January, the concentrations of glutamate, alanine, aspartate, and proline increase. For this time period, a rise in the intensity of the cell metabolic activity and photosynthesis in *F. vesiculosus* was revealed (Kuznetsov & Schoschina, 2003 ; Ryzhik, 2016). Apparently, a rise in the FAA content is related to the preparation for the intensive alga growth since FAA are involved in building proteins. Probably, the FAA stock at the early growth period will contribute to a more intensive growth of the alga thallus area under low environmental temperatures. The nature of the FAA change in January–March coincides with the alga preparation for the growth period and transition from the dormancy phase to the growth one. This period can be considered as the **growth activation phase**.

The **growth phase** of *F. vesiculosus* lasts from March to June and is characterized by a maximum growth rate of the alga thalli, intensive development of receptacles, and maximum values of the intensity of photosynthesis (April–May) (Kuznetsov & Schoschina, 2003 ; Makarov et al., 1995). During this period, there is a significant rise in the cell metabolic activity indicating active growth processes (Ryzhik, 2016). Plant growth is associated with a considerable need for nitrogen – a part of the amino acids and, subsequently, of proteins required for building new cells. In *F. vesiculosus*, the meristematic tissue is located in the apical areas of the thallus. As shown for *Fucus* species, photoassimilates, *inter alia* FAA, are transported to apical areas of the thallus from its middle part (Diouris, 1989 ; Diouris & Floc'h, 1984). In brown algae, the rate of photoassimilate outflow into the growth area depends on a growth rate of the thallus (Lüning et al., 1973). As revealed, the beginning of intensive growth and, as a result, the FAA outflow from the middle part of the thallus into the apical areas depends on environmental temperature and can shift closer to summer in algae growing under lower temperatures (Klindukh & Obluchinskaya, 2018). Apparently, a sharp decrease in the FAA content in April results from the onset of the intensive growth and an outflow of accumulated FAA from the middle part of the thallus

to the apical areas. The main participants of redistribution and transport of nitrogen along *F. vesiculosus* thallus seem to be glutamic and aspartic acids, as well as proline and alanine. In brown algae, glutamate, aspartate, alanine, serine, and glycine are known to act as a transport form of nitrogen along the thallus (Diouris, 1989 ; Schmitz et al., 1972 ; Schmitz & Srivastava, 1979). In May and June, the content of glutamate and aspartate increased significantly after a decrease in April, despite the continued growth of the alga thalli. This may indicate a gradual decrease in a growth rate and a drop in a need for amino acids. Moreover, this can be considered as an adaptation to the summer nitrogen deficiency in the environment.

The algae of the southern bend of the Kola Bay do not experience a lack of nitrogen throughout the year, but the competition for nitrogen increases greatly in late spring and in summer, and this results in a decrease in its concentration in water (Kola Bay, 1997). In the thallus of the Barents Sea *F. vesiculosus*, nitrogen is mostly represented by organic compounds of a protein nature (Barashkov et al., 1966). As shown, algae are able to accumulate FAA at high concentrations of inorganic forms of nitrogen in water and to use them as reserve forms of nitrogen during its low concentrations (Angell et al., 2014 ; Naldi & Wheeler, 1999 ; Park et al., 2013). This provides high growth rates and a possibility of forming a larger number of reproductive cells (spores and gametes).

The **storage phase** in *F. vesiculosus* begins in July and lasts until September. During this period, the alga completes its vegetative development; release of reproductive cells occurs, as well as restructuring of metabolism and growth processes towards preparation for winter (Kuznetsov & Schoschina, 2003 ; Ryzhik, 2016). In August, the second peak in dynamics of the cell metabolic activity is recorded (Ryzhik, 2016), and the content of dry matter, alginates, and fucoidan increases (Obluchinskaya et al., 2002). In the storage phase, the FAA content in *F. vesiculosus* decreases. Out of prevailing amino acids, a drop was revealed in glutamate, aspartate, and alanine. The concentration of proline, on the contrary, slightly increased. During this period, FAA can be spent on the processes of growth and maturation of reproductive cells. Apparently, in the considered developmental phase, the FAA synthesis and protein formation in *F. vesiculosus* slow down; this may be due to a need for accumulating reserve substances and the orientation of metabolism towards the synthesis of carbohydrates rather than nitrogen-containing substances. The decrease in the FAA content is also associated with the use of internal reserves of amino acids during this period since the content of inorganic forms of nitrogen in the environment decreases (Kola Bay, 1997). A slight rise in proline in the storage phase can be caused by temperature fluctuations and periodic desalination due to precipitation during low tides. Proline is known to be involved in osmoregulation processes; it contributes to plant resistance to low temperatures (Munns, 2005 ; Naidu et al., 1991 ; Trovato et al., 2008). An experiment with the green alga *Ulva pertusa* Kjellman, 1897 showed that significant temperature fluctuations stimulate an increase in the content of free proline and slow down the plant growth (Wang Q. et al., 2007).

The seasonal dynamics of the FAA content in *F. vesiculosus* is similar to that in the White Sea *Fucus* sp., the Far Eastern *Laminaria japonica* Areschoug, 1851, the red alga *Gracilaria vermiculophylla* (Ohmi) Papenfuss, 1967 from the coast of France, the Antarctic brown alga *Ascoseira mirabilis* Skottsberg, 1907, and the green alga *Prasiola crispa* (Lightfoot) Kützing, 1843 (Krupnova, 2002 ; Repina, 2005 ; Gomez & Wiencke, 1998 ; Jackson & Seppelt, 1995 ; Surget et al., 2017). The listed algae are also characterized by prevalence of glutamate, aspartate, alanine, proline, threonine, glycine, and taurine in the FAA pool. In the Scottish *Palmaria palmata* (Linnaeus) F. Weber & D. Mohr, 1805, algae from the southern coast of the Mediterranean Sea, and the Sea of Japan brown

alga *Sargassum fusiforme* (Harvey) Setchell, 1931, the reverse trend of the FAA accumulation was observed – high content in the autumn–winter period and low content during spring–summer (Khaleafa et al., 1982 ; Mohsen et al., 1975 ; Morgan et al., 1980 ; Nagahisa et al., 1994). Seasonal differences in the accumulation and decrease of FAA in algae depend on both external environmental factors and a direction of metabolic processes in a certain developmental phase. The FAA accumulation in autumn–winter may be related to the occurrence of vegetative or generative cycle of algae development during this period, as well as to participation of amino acids in the protection of cellular structures under sub-zero temperatures (Jackson & Seppelt, 1995 ; Morgan et al., 1980 ; Nagahisa et al., 1994).

The onset of the developmental phases is largely determined by external factors. Low water and air temperatures, as well as cloudiness reducing irradiance, delay the beginning of the vegetation period in spring. Importantly, a delay in the beginning of intensive vegetation due to low water temperatures results in a shift in the release of reproductive cells in summer (Kuznetsov & Schoschina, 2003).

Changes in the FAA content in *F. vesiculosus* were affected by both the general direction of metabolic processes in a certain developmental phase and environmental conditions. The one-way analysis of variance revealed the effect of seawater salinity, air temperature, and water temperature on the FAA content in *F. vesiculosus* thallus. The correlation coefficients have a positive linear relationship between water and air temperatures and the content of arginine, aspartate, glutamate, and methionine. Those have a negative linear relationship between the salinity of seawater and the content of arginine, aspartate, histidine, glutamate, and hydroxyproline. The total amount of FAA is also linearly dependent on air temperature and water salinity (Table 4).

Table 4. Values of the Pearson correlation coefficient between the concentration of free amino acids and external environmental conditions ($n = 44$; $p \leq 0.05$)

Amino acid	Water temperature, °C	Air temperature, °C	Water salinity, ‰
Arginine	**0.60**	**0.62**	**–0.52**
Aspartic acid	**0.66**	**0.58**	**–0.71**
Histidine	0.33	0.39	**–0.55**
Glutamic acid	0.41	**0.56**	**–0.73**
Methionine	**0.56**	0.49	–0.41
Hydroxyproline	0.26	0.46	**–0.71**
Total amount of FAA	0.40	**0.57**	**–0.74**

Note: values in bold indicate medium to high correlation between variables.

For most algae of the Barents Sea, the optimal growth temperature is +10…+15 °C (Voskoboinikov et al., 2015). In general, the content of most FAA and their total amount in *F. vesiculosus* is higher at temperatures optimal for growth (Tables 2 and 4, Fig. 1). The exception is March, with high FAA content at low temperatures. This is probably due to the FAA accumulation in the middle part of the thallus *prior* to the beginning of growth and their use as structural substances during the intensive growth. An increase in the FAA content within a certain temperature range indicates that the intensity of the synthesis of these compounds is higher than the rates of their catabolism. These ranges vary for different algal species. Specifically, in the green alga *Ulva fasciata* Delile, 1813, the highest FAA content was recorded at the optimal growth temperature of +25 °C (Mohsen et al., 1973). In *U. pertusa*, a rise in water temperature, optimal for the growth, by 10 °C resulted in a 2.2-fold increase in the FAA content (Kakinuma et al., 2006). In the Antarctic green alga *P. crispa* and the northern Atlantic red alga

Mastocarpus stellatus (Stackhouse) Guiry, 1984, the content of free proline increases during cold periods (Harris & Logan, 2018 ; Jackson & Seppelt, 1995). In these species, the amount of free proline significantly rises as the environmental temperature drops below the freezing point of the cytoplasm in cells: for *P. crispa* and *M. stellatus*, free proline acts as a cryoprotectant and increases resistance to freezing. In *F. vesiculosus*, with a significant drop in environmental temperature in January 2016, the content of FAA, *inter alia* free proline, decreased (Table 1, Fig. 1). Thus, FAA are not directly involved in the protection of the alga from sub-zero temperatures, but those may be precursors in the synthesis of cryoprotectants during cold season.

The highest concentrations of proline and alanine were recorded in March. This is probably due to the fact that these amino acids not only are accumulated as structural components for building proteins but are involved in protective reactions of algae in response to adverse external factors. In autumn and spring, an increase in the concentration of proline and alanine may be related to fluctuations in environmental temperature and irradiance. Low temperatures combined with high irradiance can contribute to an increase in the content of reactive oxygen species. Proline and alanine are capable of acting as antioxidants. As known, free proline in plant cells is involved in inactivation of reactive oxygen species which are formed under various stress effects (Kaul et al., 2008 ; Matysik et al., 2002 ; Saradhi et al., 1995).

Negative correlation between the concentrations of glutamate, aspartate, arginine, histidine, and hydroxyproline and water salinity indicates that this factor has a positive effect on the accumulation of these amino acids under low salinity. Lack of a linear relationship between the concentrations of other FAA and water salinity evidences that it is not a decisive factor for their content. Its effect is manifested only within a complex of environmental factors. According to previous studies on *F. vesiculosus* from natural populations, the content of free proline and other FAA depends on water salinity in the species habitats. The concentration of free proline increased in the algae thalli from low salinity areas (Klindukh et al., 2011). A spring decrease in water salinity had different effects on the FAA content in different parts of the thallus (Klindukh & Obluchinskaya, 2018).

Changes in the FAA content in algae in response to a decrease in water salinity largely depend on the species peculiarities and on the duration of the effect. Specifically, in *U. pertusa* and *Pyropia haitanensis* (T. J. Chang & B. F. Zheng) N. Kikuchi & M. Miyata, 2011, exposure to low-salinity seawater resulted in a decrease in the content of free proline; in *Gracilaria corticata* (J. Agardh) J. Agardh, 1852, on the contrary, such an exposure caused a 2-fold rise (Kakinuma et al., 2006 ; Kumar et al., 2010 ; Wang W. et al., 2020). The content of other free amino acids in algae changes during low salinity as well. The effect of water of 4 ‰ led to a decrease in the content of prevailing FAA in *Ectocarpus siliculosus* (Dillwyn) Lyngbye, 1819; at the same time, the concentration of aromatic amino acids and branched-chain amino acids increased (Dittami et al., 2011). In *Cladophora vagabunda* (Linnaeus) Hoek, 1963, reduction of habitat salinity caused a rise in glutamate and lysine and a drop in aspartate, threonine, valine, arginine, glycine, and histidine (Rani, 2007).

F. vesiculosus is found on the Barents Sea coast both in areas with oceanic salinity and in gulfs and bays with constant low salinity (Malavenda & Voskoboinikov, 2008). Waters with a salinity of 25.5–34 ‰ and 17 ‰ are considered optimal for growth of algae from marine and brackish-water populations, respectively (Voskoboinikov et al., 2015). *F. vesiculosus* inhabiting the littoral in the Abram-Mys area is constantly exposed to low salinity. For this alga, water of 15–20 ‰ is optimal for growth and has no stressful effect on metabolism.

During the period of minimum water salinity recorded, the content of most FAA and their total amount in *F. vesiculosus* thalli was the highest throughout the year. In late spring and early summer, the FAA accumulation occurs due to the storage of nitrogen required for growth and reproduction in the summer season when its content in the environment decreases. Apparently, a severe drop in seawater salinity can contribute to an increase in the FAA content during this period reducing the intensity of protein synthesis and, accordingly, affecting the intensity of alga growth, as well as contributing to a rise in amino acid biosynthesis. Reduced salinity is known to slow down a growth rate of length and mass of *F. vesiculosus* thalli and to cause an increase in the amount of individual total amino acids in the alga (Munda & Garrasi, 1978 ; Nygard & Dring, 2008).

Conclusion. The qualitative composition of free amino acids in *F. vesiculosus* did not change throughout the year. Glutamic and aspartic acids, alanine, and proline prevailed in the FAA pool. Changes in the FAA concentration have a clearly pronounced annual dynamics which coincides with the main developmental phases of the alga. Higher concentrations are typical for most FAA in the spring–summer period, and lower content is typical in autumn–winter. The FAA dynamics in different developmental phases of *F. vesiculosus* was associated with processes occurring in the alga; it is affected by growth rate, cell metabolic activity, photosynthesis rate, and generative development. Each developmental phase is characterized by its own dynamics of the FAA content. Based on the analysis of the FAA concentration, as well as literature data on the dynamics of other physiological parameters (growth rate and cell metabolic activity), the following phases of *F. vesiculosus* development were distinguished: dormancy, growth activation, growth, and storage. An analysis of the effect of environmental factors on the FAA content allowed to assume the participation of FAA in the formation of the alga adaptation to fluctuations in salinity and temperature of the environment. Apparently, in the brown alga, glutamic and aspartic acids, which are accumulated in the middle part of the thallus in May–June, act as one of the reserve organic forms of nitrogen. Probably, the transport of organic forms of nitrogen in *F. vesiculosus* thallus is carried out by glutamate, aspartate, alanine, and proline.

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REFERENCES

1. Barashkov G. K., Vakhrashina A. V., Petrov Yu. E. Sezonnye izmeneniya khimicheskogo sostava u fukusovykh vodoroslei Barentseva morya Kol'skogo poluostrova. *Rastitel'nye resursy*, 1966, vol. 2, iss. 2, pp. 191–200. (in Russ.)
2. Voskoboinikov G. M., Makarov M. V., Malavenda S. V., Ryzhik I. V. Adaptation and regulation of growth of macroohytes in the Barents Sea. *Vestnik Kol'skogo nauchnogo tsentra RAN. Estestvennye i tekhnicheskie nauki*, 2015, no. 2 (21), pp. 40–48. (in Russ.)
3. GOST 26185-84. *Vodorosli morskie, travy morskie i produkty ikh pererabotki. Metody analiza.* Moscow : Izd-vo standartov, 2004, 34 p. (in Russ.)
4. *The Kola Bay: Oceanography, Biology, Ecosystems, Pollutants* / G. G. Matishov (Ed.) ; Murmansk Mar. Biol. Inst. KSC RAS. Apatity : KNTs RAN, 1997, 265 p. (in Russ.)
5. *Kola Bay: Development and Rational Nature Management* / G. G. Matishov (Ed.) ; Murmansk Mar. Biol. Inst. KSC RAS. Moscow : Nauka, 2009, 381 p. (in Russ.)
6. Krupnova T. N. Osobennosti razvitiya sporonosnoi tkani u laminarii yaponskoi pod vozdeistviem izmenyayushchikhsya uslovii sredy. *Izvestiya TINRO*, 2002, vol. 130, no. 2, pp. 474–482. (in Russ.)
7. Kuznetsov L. L., Schoschina E. V. *Phytocenoses of the Barents Sea (Physiological and Structural*

Characteristics). Apatity : KNTs RAN, 2003, 308 p. (in Russ.)
8. Malavenda S. V., Voskoboinikov G. M. Influence of abiotic factors on the structure of brown alga *Fucus vesiculosus* population in East Murman (Barents Sea). *Biologiya morya*, 2008, vol. 34, no. 1, pp. 30–34. (in Russ.)
9. *Metody fiziologo-biokhimicheskogo issledovaniya vodoroslei v gidrobiologicheskoi praktike* / A. V. Topachevsky (Ed.). Kyiv : Naukova dumka, 1975, 248 p. (in Russ.)
10. Repina O. I. Fukoidy Belogo morya: khimicheskii sostav i perspektivy ispol'zovaniya. In: *Morskie pribrezhnye ekosistemy: Vodorosli, bespozvonochnye i produkty ikh pererabotki* : materialy II nauch.-prakt. konf., Arkhangelsk, 4–7 Oct., 2005. Moscow : VNIRO, 2005, pp. 216–219. (in Russ.)
11. Rudenko A. O., Kartsova L. A., Snarskiy S. I. Opredelenie vazhneishikh aminokislot v slozhnykh ob"ektakh biologicheskogo proiskhozhdeniya metodom obrashchenno-fazovoi VEZhKh s polucheniem feniltiogidantoinov aminokislot. *Sorbtsionnye i khromatograficheskie protsessy*, 2010, vol. 10, iss. 2, pp. 223–230. (in Russ.)
12. Ryzhik I. V. Fotosinteticheskaya aktivnost' *Fucus vesiculosus* L. i *Fucus distichus* L. Barentseva morya posle polyarnoi nochi. In: *Materialy XXV konferentsii molodykh uchenykh MMBI*. Apatity : KNTs RAN, 2007, pp. 177–182. (in Russ.)
13. Angell A. R., Mata L., de Nys R., Paul N. A. Variation in amino acid content and its relationship to nitrogen content and growth rate in *Ulva ohnoi* (Chlorophyta). *Journal of Phycology*, 2014, vol. 50, iss. 1, pp. 216–226. https://doi.org/10.1111/jpy.12154
14. Diouris M. Long-distance transport of ^{14}C-labelled assimilates in the Fucales: Nature of translocated substances in *Fucus serratus*. *Phycologia*, 1989, vol. 28, iss. 4, pp. 504–511. https://doi.org/10.2216/i0031-8884-28-4-504.1
15. Diouris M., Floc'h J. Y. Long-distance transport of C-labelled assimilates in the Fucales: Directionality, pathway and velocity. *Marine Biology*, 1984, vol. 78, pp. 199–204. https://doi.org/10.1007/BF00394701
16. Dittami S. M., Gravot A., Renault D., Goulitquer S., Eggert A., Bouchereau A., Boyen C., Tonon T. Integrative analysis of metabolite and transcript abundance during the short-term response to saline and oxidative stress in the brown alga *Ectocarpus siliculosus*. *Plant, Cell and Environment*, 2011, vol. 34, iss. 4, pp. 629–642. https://doi.org/10.1111/j.1365-3040.2010.02268.x
17. Galili G., Höfgen R. Metabolic engineering of amino acids and storage proteins in plants. *Metabolic Engineering*, 2002, vol. 4, iss. 1, pp. 3–11. https://doi.org/10.1006/mben.2001.0203
18. Gomez I., Wiencke C. Seasonal changes in C, N and major organic compounds and their significance to morpho-functional processes in the endemic Antarctic brown alga *Ascoseira mirabilis*. *Polar Biology*, 1998, vol. 19, pp. 115–124. https://doi.org/10.1007/s003000050222
19. Harris J. P., Logan B. A. Seasonal acclimatization of thallus proline contents of *Mastocarpus stellatus* and *Chondrus crispus*: Intertidal rhodophytes that differ in freezing tolerance. *Journal of Phycology*, 2018, vol. 54, iss. 3, pp. 419–422. https://doi.org/10.1111/jpy.12624
20. Hildebrandt T. M., Nunes Nesi A., Araujo W. L., Braun H.-P. Amino acid catabolism in plants. *Molecular Plant*, 2015, vol. 8, iss. 11, pp. 1563–1579. https://doi.org/10.1016/j.molp.2015.09.005
21. Jackson A. E., Seppelt R. D. The accumulation of proline in *Prasiola crispa* during winter in Antarctica. *Physiologia Plantarum*, 1995, vol. 94, iss. 1, pp. 25–30. https://doi.org/10.1111/j.1399-3054.1995.tb00779.x
22. Kakinuma M., Coury D. A., Kuno Y., Itoh S., Kozawa Y., Inagaki E., Yoshiura Y., Amano H. Physiological and biochemical responses to thermal and salinity stresses in a sterile mutant of *Ulva pertusa* (Ulvales, Chlorophyta). *Marine Biology*, 2006, vol. 149, pp. 97–106. https://doi.org/10.1007/s00227-005-0215-y
23. Kaul S., Sharma S. S., Mehta I. K. Free radical scavenging potential of L-proline: Evidence from *in vitro* assays. *Amino*

Acids, 2008, vol. 34, iss. 2, pp. 315–320. https://doi.org/10.1007/s00726-006-0407-x

24. Khaleafa A. F., Mohsen A. F., Shaalan S. H. Seasonal variations in the growth and amino acid pattern of *Caulerpa prolifera* (Foerskal) Lamouroux. *Hydrobiological Bulletin*, 1982, vol. 16, iss. 2–3, pp. 201–206. https://doi.org/10.1007/BF02255373
25. Klindukh M. P., Obluchinskaya E. D., Matishov G. G. Seasonal changes in the mannitol and proline contents of the brown alga *Fucus vesiculosus* L. on the Murman coast of the Barents Sea. *Doklady Biological Sciences*, 2011, vol. 441, pp. 373–376. https://doi.org/10.1134/s0012496611060032
26. Klindukh M. P., Obluchinskaya E. D. A comparative study of free amino acids of the brown alga *Fucus vesiculosus* Linnaeus, 1753 from the intertidal zone of the Murman shore, Barents Sea. *Russian Journal of Marine Biology*, 2018, vol. 44, iss. 3, pp. 232–239. https://doi.org/10.1134/S1063074018030069
27. Kumar M., Kumari P., Gupta V., Reddy C. R. K., Jha B. Biochemical responses of red alga *Gracilaria corticata* (Gracilariales, Rhodophyta) to salinity induced oxidative stress. *Journal of Experimental Marine Biology and Ecology*, 2010, vol. 391, iss. 1–2, pp. 27–34. https://doi.org/10.1016/j.jembe.2010.06.001
28. Lam H. M., Hsieh M. H., Coruzzi G. Reciprocal regulation of distinct asparagine synthetase genes by light and metabolites in *Arabidopsis thaliana*. *Plant Journal*, 1998, vol. 16, iss. 3, pp. 345–353. https://doi.org/10.1046/j.1365-313x.1998.00302.x
29. Lüning K., Schmitz K., Willenbrink J. CO_2 fixation and translocation in benthic marine algae. III. Rates and ecological significance of translocation in *Laminaria hyperborea* and *L. saccharina*. *Marine Biology*, 1973, vol. 23, iss. 4, pp. 275–281. https://doi.org/10.1007/BF00389334
30. Maehre H. K., Malde M. K., Eilertsen K. E., Elvevoll E. O. Characterization of protein, lipid and mineral contents in common Norwegian seaweeds and evaluation of their potential as food and feed. *Journal of the Science of Food and Agriculture*, 2014, vol. 94, iss. 15, pp. 3281–3290. https://doi.org/10.1002/jsfa.6681
31. Makarov V. N., Schoschina E. V., Lüning K. Diurnal and circadian periodicity of mitosis and growth in marine macroalgae. I. Juvenile sporophytes of Laminariales (Phaeophyta). *European Journal of Phycology*, 1995, vol. 30, iss. 4, pp. 261–270. https://doi.org/10.1080/09670269500651031
32. Makarov M. V., Ryzhik I. V., Voskoboinikov G. M., Matishov G. G. The effect of *Fucus vesiculosus* L. location in the depth on its morphophysiological parameters in the Barents Sea. *Doklady Biological Sciences*, 2010, vol. 430, iss. 1, pp. 39–41. https://doi.org/10.1134/S0012496610010138
33. Matysik J., Alia, Bhalu B., Mohanty P. Molecular mechanisms of quenching of reactive oxygen species by proline under stress in plants. *Current Science*, 2002, vol. 82, no. 5, pp. 525–532.
34. Mohsen A. F., Nasr A. H., Metwalli A. M. Effect of different light intensities on growth, reproduction, amino acid synthesis, fat and sugar contents in *Ulva fasciata* Delile. *Hydrobiologia*, 1973, vol. 43, iss. 1–2, pp. 125–135. https://doi.org/10.1007/BF00014261
35. Mohsen A. F., Kharboush A. M., Khaleafa A. F., Metwalli A., Azab Y. Amino acid pattern and seasonal variation in some marine algae from Alexandria. *Botanica Marina*, 1975, vol. 18, iss. 3, pp. 167–178. https://doi.org/10.1515/botm.1975.18.3.167
36. Morgan K. C., Wright J. L. C., Simpson F. J. Review of chemical constituents of the red alga *Palmaria palmata* (dulse). *Economic Botany*, 1980, vol. 34, iss. 1, pp. 27–50. https://doi.org/10.1007/BF02859553
37. Mouritsen O. G., Duelund L., Petersen M. A., Hartmann A. L., Frøst M. B. Umami taste, free amino acid composition, and volatile compounds of brown seaweeds. *Journal of Applied Phycology*, 2019, vol. 31, iss. 2, pp. 1213–1232. https://doi.org/10.1007/s10811-018-1632-x
38. Munda I. M., Garrasi C. Salinity-induced changes of nitrogenous constituents in *Fucus vesiculosus* (Phaeophyceae). *Aquatic Botany*, 1978,

vol. 4, pp. 347–351. https://doi.org/10.1016/0304-3770(78)90031-1

39. Munns R. Genes and salt tolerance: Bringing them together. *New Phytologist*, 2005, vol. 167, iss. 3, pp. 645–663. https://doi.org/10.1111/j.1469-8137.2005.01487.x
40. Naidu B. P., Paleg L. G., Aspinall D., Jennings A. C., Jones G. P. Amino acid and glycine betaine accumulation in cold-stressed wheat seedlings. *Phytochemistry*, 1991, vol. 30, iss. 2, pp. 407–409. https://doi.org/10.1016/0031-9422(91)83693-F
41. Nagahisa E., Kanno N., Sato M., Sato Y. Variations in D-aspartate content with season and part of *Hizikia fusiformis*. *Fisheries Science*, 1994, vol. 60, iss. 6, pp. 777–779. https://doi.org/10.2331/fishsci.60.777
42. Naldi M., Wheeler P. A. Changes in nitrogen pools in *Ulva fenestrata* (Chlorophyta) and *Gracilaria pacifica* (Rhodophyta) under nitrate and ammonium enrichment. *Journal of Phycology*, 1999, vol. 35, iss. 1, pp. 70–77. https://doi.org/10.1046/j.1529-8817.1999.3510070.x
43. Nygard C. A., Dring M. J. Influence of salinity, temperature, dissolved inorganic carbon and nutrient concentration on the photosynthesis and growth of *Fucus vesiculosus* from the Baltic and Irish seas. *European Journal of Phycology*, 2008, vol. 43, iss. 3, pp. 253–262. https://doi.org/10.1080/09670260802172627
44. Obluchinskaya E. D., Voskoboinikov G. M., Galynkin V. A. Contents of alginic acid and fucoidan in *Fucus* algae of the Barents Sea. *Applied Biochemistry and Microbiology*, 2002, vol. 38, pp. 186–188. https://doi.org/10.1023/A:1014374903448
45. Oliveira I. C., Coruzzi G. Carbon and amino acids reciprocally modulate the expression of glutamine synthetase in *Arabidopsis*. *Plant Physiology*, 1999, vol. 221, iss. 1, pp. 301–309. https://doi.org/10.1104/pp.121.1.301
46. Park C. S., Park K. Y., Hwang E. K., Kakinuma M. Effects of deep seawater medium on growth and amino acid profile of a sterile *Ulva pertusa* Kjellman (Ulvaceae, Chlorophyta). *Journal of Applied Phycology*, 2013, vol. 25, iss. 3, pp. 781–786. https://doi.org/10.1007/s10811-013-9985-7
47. Parthasarathy A., Cross P. J., Dobson R. C., Adams L. E., Savka M. A., Hudson A. O. A three-ring circus: Metabolism of the three proteogenic aromatic amino acids and their role in the health of plants and animals. *Frontiers in Molecular Biosciences*, 2018, vol. 5, art. no. 29 (30 p.). https://doi.org/10.3389/fmolb.2018.00029
48. Peinado I., Giron J., Koutsidis G., Ames J. M. Chemical composition, antioxidant activity and sensory evaluation of five different species of brown edible seaweeds. *Food Research International*, 2014, vol. 66, pp. 36–44. https://doi.org/10.1016/j.foodres.2014.08.035
49. Rani G. Changes in protein profile and amino acids in *Cladophora vagabunda* (Chlorophyceae) in response to salinity stress. *Journal of Applied Phycology*, 2007, vol. 19, pp. 803–807. https://doi.org/10.1007/s10811-007-9211-6
50. Rhodes D., Hanson A. D. Quaternary ammonium and tertiary sulfonium compounds in higher plants. *Annual Review of Plant Physiology and Plant Molecular Biology*, 1993, vol. 44, pp. 357–384. https://doi.org/10.1146/annurev.pp.44.060193.002041
51. 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, pp. 433–436. https://doi.org/10.1134/S1063074016050102
52. Ryzhik I. V., Kosobryukhov A. A., Markovskaya E. F., Makarov M. V. Photosynthetic capacity of *Fucus vesiculosus* Linnaeus, 1753 (Phaeophyta: Fucales) in the Barents Sea during the tidal cycle. *Biology Bulletin*, 2021, vol. 48, pp. 48–56. https://doi.org/10.1134/S1062359020060114
53. Saradhi P. P., AliaArora S., Prasad K. V. S. K. Proline accumulates in plants exposed to UV radiation and protects them against UV-induced peroxidation. *Biochemical and Biophysical Research Communications*, 1995, vol. 209, iss. 1, pp. 1–5. https://doi.org/10.1006/bbrc.1995.1461

54. Schmitz K., Lüning K., Willenbrink J. CO_2-Fixierung und Stofftransport in benthischen marinen Algen. II. Zum Ferntransport ^{14}C-markierter assimilate bei *Laminaria hyperborea* und *Laminaria saccharina*. *Zeitschrift für Pflanzenphysiologie*, 1972, vol. 67, iss. 5, pp. 418–429. https://doi.org/10.1016/S0044-328X(72)80042-4
55. Schmitz K., Srivastava L. M. Long distance transport in *Macrocystis integrifolia*. I. Translocation of ^{14}C-labelled assimilates. *Plant Physiology*, 1979, vol. 63, iss. 6, pp. 995–1022. https://doi.org/10.1104/pp.63.6.995
56. Stewart G. R., Larher F. Accumulation of amino acids and related compounds in relation to environmental stress. In: *The Biochemistry of Plants: A Comprehensive Treatise*. Vol. 5. *Amino Acids and Derivatives* / B. J. Miflin (Ed.). New York ; London : Academic Press, 1980, pp. 609–635. https://doi.org/10.1016/b978-0-12-675405-6.50023-1
57. Surget G., Le Lann K., Delebecq G., Kervarec N., Donval A., Poullaouec M.-A., Bihannic I., Poupart N., Stiger-Pouvreau V. Seasonal phenology and metabolomics of the introduced red macroalga *Gracilaria vermiculophylla*, monitored in the Bay of Brest (France). *Journal of Applied Phycology*, 2017, vol. 29, pp. 2651–2666. https://doi.org/10.1007/s10811-017-1060-3
58. Tropin I. V., Radzinskaya N. V., Voskoboinikov G. M. The influence of salinity on the rate of dark respiration and structure of the cells of brown algae thalli from the Barents Sea littoral. *Biology Bulletin*, 2003, vol. 30, no. 1, pp. 40–47. https://doi.org/10.1023/A:1022063426675
59. Trovato M., Mattioli R., Costantino P. Multiple roles of proline in plant stress tolerance and development. *Rendiconti Lincei*, 2008, vol. 19, pp. 325–346. https://doi.org/10.1007/s12210-008-0022-8
60. Wang Q., Dong S., Tian X., Wang F. Effects of circadian rhythms of fluctuating temperature on growth and biochemical composition of *Ulva pertusa*. *Hydrobiologia*, 2007, vol. 586, pp. 313–319. https://doi.org/10.1007/s10750-007-0700-z
61. Wang W., Chen T., Xu Y., Xu K., Ji D., Chen C., Xie C. Investigating the mechanisms underlying the hyposaline tolerance of intertidal seaweed, *Pyropia haitanensis*. *Algal Research*, 2020, vol. 47, art. no. 101886 (12 p.). https://doi.org/10.1016/j.algal.2020.101886
62. Zrenner R., Stitt M., Sonnewald U., Boldt R. Pyrimidine and purine biosynthesis and degradation in plants. *Annual Review of Plant Biology*, 2006, vol. 57, pp. 805–836. https://doi.org/10.1146/annurev.arplant.57.032905.105421

ДИНАМИКА СОДЕРЖАНИЯ СВОБОДНЫХ АМИНОКИСЛОТ В БУРОЙ ВОДОРОСЛИ *FUCUS VESICULOSUS* LINNAEUS, 1753 БАРЕНЦЕВА МОРЯ В ТЕЧЕНИЕ ГОДА

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Свободные аминокислоты (САК) являются важными биохимическими соединениями любой клетки. Их состав и содержание зависят от физиологического состояния, абиотических факторов среды и фазы развития организма. Функции САК в растениях очень разнообразны и включают участие не только в синтезе белков и других соединений, но и в адаптации водорослей к неблагоприятным условиям среды. Сведения о динамике САК важны для понимания их роли в формировании устойчивости водорослей к меняющимся факторам среды. Цель данного исследования — определить содержание САК в бурой водоросли *Fucus vesiculosus*

и их сезонные изменения и выявить зависимости от факторов среды и фазы развития фукуса. Водоросли для изучения собирали на литорали Кольского залива Баренцева моря в период отлива раз в месяц с декабря 2015 г. по декабрь 2016 г. Для исследования использовали среднюю часть таллома. Качественный и количественный состав САК определяли методом высокоэффективной жидкостной хроматографии. Качественный состав САК в течение года не изменялся; доминирующими в пуле САК были глутаминовая и аспарагиновая кислоты, аланин и пролин. Содержание САК изменялось в течение года; максимальное количество отмечено в весенне-летний период. Содержание САК зависело от внешних факторов среды. Определены корреляционные зависимости между концентрациями отдельных САК и температурой воздуха, температурой и солёностью воды. Динамика САК в разные фазы развития фукуса связана с происходящими в водорослях процессами; на неё влияют скорость роста, клеточная метаболическая активность, скорость фотосинтеза и генеративное развитие. Для каждой из фаз развития характерна своя динамика содержания САК. На основании динамики концентрации САК у фукуса найдены соответствия с фазами развития (покоя, активации роста, роста, накопления запасных веществ). В качестве одного из резервных источников органического азота у фукуса, возможно, выступают свободный глутамат и аспартат. Транспорт органических форм азота в талломе фукуса, вероятно, осуществляется за счёт глутамата, аспартата, аланина и пролина.

Ключевые слова: *Fucus vesiculosus*, свободные аминокислоты, сезонные изменения, фазы развития, температура, солёность, Баренцево море