ИнБЮМ – IBSS

Морской биологический журнал
Marine Biological Journal
2025, vol. 10, no. 2, pp. 3–17
https://marine-biology.ru

SCIENTIFIC COMMUNICATIONS

UDC [574.5:[582.272:661.635]](262.5)

MACROPHYTOCENOSES AS BIOGEOCHEMICAL BARRIERS TO WATER HYPEREUTROPHICATION BY MINERAL PHOSPHORUS OFF THE SOUTHWESTERN CRIMEA

© 2025 **V. Egorov, N. Milchakova, N. Bobko, and Yu. Marchenko**

A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS, Sevastopol, Russian Federation
E-mail: *egorov@ibss-ras.ru*

Received by the Editor 30.07.2024; after reviewing 16.01.2025;
accepted for publication 20.03.2025.

The aim of the work was to study mineral phosphorus concentration by brown algae *Cystoseira crinita* and *Cystoseira barbata* listed in the Red Book of the Republic of Crimea and to assess the role of macrophytobenthos in the coastal ecosystem of the Southwestern Crimea in formation of biogeochemical barriers that regulate competitive relations of producers for biogenic elements. As established, *Cystoseira crinita* and *Cystoseira barbata* accumulate mineral phosphorus to levels of 170.0–377.1 $\text{mg}\cdot\text{kg}^{-1}$, a mean of (224.7 ± 55.7) $\text{mg}\cdot\text{kg}^{-1}$ wet weight, with accumulation factors of 15,454–92,244 units, a mean of (35,300 ± 27,800) units. According to the updated nomenclature of the family Sargassaceae Kützing, these algae species belong to the *Ericaria*-dominated phytocenosis: *Ericaria crinita* + *Gongolaria barbata* – *Cladostephus spongiosus* – *Ellisolandia elongata* (*Ericaria* sp.). In general, brown algae of coastal biotopes uptake and retain over 80% of mineral phosphorus occurring in the aquatic environment and release back only up to 16% of maximum absorbed flux daily. This highlights their critical role in conditioning the biogenic composition of waters.

Keywords: biogenic elements, macrophytobenthos, pool of mineral phosphorus in water and algae, Southwestern Crimea, Black Sea

According to experts in environmental science, excessive influx of biogenic elements has caused hypereutrophication and a decline in water quality in the Black Sea, particularly in its coastal areas. Adverse effects of hypereutrophication on the marine ecosystem induced phytoplankton blooms, hypoxia and fish kills, outbreaks of Cyanobacteria and gelatinous plankton, reduced water transparency, increased organic matter fluxes from the photosynthetic zone, and shifts in key trophic chain balance [Fiori et al., 2016; Gubanov et al., 2004; Ivanov et al., 2006; Kuftarkova et al., 2006; Mee, 1992; Oguz, Gilbert, 2007; Yunev et al., 2019; Zaitsev et al., 1989]. Despite reduced regional economic activity in the 1990s, the Black Sea ecosystem did not return to its pre-eutrophication state [Slepchuk et al., 2017; Yunev et al., 2019]. To date, research on de-eutrophication is focused on enhancing standards to mitigate marine pollution caused by excess anthropogenic organic compounds and biogenic elements. Promising strategies in this field involve using macrophytes to reduce phytoplankton primary production. In this respect, key directions are as follows:

1) developing technologies for safe intervention in natural ecosystem functioning processes to remove the excess of biogenic elements [Kompleksnaya adaptatsiya, 1985];
2) creating geochemical barriers on biopositive surfaces to limit biogenic element availability for primary production [Aleksandrov, 2008];
3) developing methods to regulate permissible pollution limits for the marine environment based on biogeochemical criteria [Egorov, 2019, 2021; Polikarpov, Egorov, 1986].

The issue of preserving the ecological state of marine natural complexes is especially critical in the Southwestern Crimea: this area is recognized by the International Union for Conservation of Nature as both a European biodiversity hotspot and a major recreational and a tourist destination [Marine Protected Areas of the Crimea, 2015]. Consequently, 31 specially protected natural areas (hereinafter SPNAs) have been established along the Crimean coast; there, economic activities are legally restricted.

Interest in natural water self-purification driven by biogeochemical mechanisms has led to the development of a semi-empirical theory of mineral metabolism in hydrobionts [Polikarpov, Egorov, 1986] and the advanced theory on radiation and chemical homeostasis of marine ecosystems [Egorov, 2019, 2021]. The application of balance-based methods of mathematical modeling, which account for biogeochemical interactions within the ecosystems, supports the hypothesis of Academician V. Vernadsky that the reproduction of living and non-living matter simultaneously sustains their habitat conditions [Vernadsky, 1965]. This has enabled the development of methods to regulate thresholds for permissible anthropogenic load based on biogeochemical criteria: ecological capacity of marine ecosystems [Polikarpov, Egorov, 1981] and their assimilative capacity [Egorov, 2019, 2021; Izrael, Tsyban, 1983].

As established, the concentration of nearly all chemical substances in both living and abiotic components of ecosystems depends on their specific content in water [Polikarpov, 1964]. Concentration functions of hydrobionts are mediated by physicochemical forms of absorbed substances, with sorption, metabolic, and trophic interactions, and also reactions of their mineral and energy metabolism. These interactions are generally governed by the principles of water mineralization, Stokes' law, Freundlich and Langmuir models, Monod equation, and Michaelis–Menten kinetics, as well as the energetic aspects of trophodynamics [Polikarpov, Egorov, 1986; Popovichev, Egorov, 2009]. As known from the literature, the primary production–limiting biogenic elements are nitrogen and phosphorus [Redfield, 1958]. According to modern concepts [Zilov, 2009], the production of 1,000 g of primary organic matter requires 80 g of carbon, 14 g of nitrogen, and 2 g of phosphorus. The limiting factor in production is the biogenic element, proportion of which is lower in the aquatic environment compared to the stoichiometric ratio $N : P = 16 : 1$ (molar concentration) or $N : P = 7 : 1$ (by mass). If the ratio exceeds this value, the system is phosphorus-limited; if it is lower, the system is nitrogen-limited. Evidently, the availability of biogenic elements for sustaining primary production depends on their dissolved forms in the aquatic environment. Their pools in other biotopes act as barriers to water eutrophication. Therefore, assessing the contribution of individual biocenoses to the formation of biogenic element pools allows for an evaluation of their barrier role in mitigating eutrophication and competitive relations of producers in coastal photic zones.

Within the framework of this study, the authors aimed to assess pools of biogenic elements in macrophytocenoses by examining the accumulation patterns of mineral phosphorus in brown algae from coastal waters of the Southwestern Crimea. The research was focused on the Streletskaya Bay (Sevastopol) inhabited by brown algae *Cystoseira crinita* and *Cystoseira barbata* listed in the Red Book of the Republic of Crimea [2015], as well as macrophytobenthos and *Ericaria*-dominated phytocenosis, *Ericaria crinita* + *Gongolaria barbata* – *Cladostephus spongiosus* – *Ellisolandia elongata*, in coastal zones of SPNAs, the Sevastopol Bay, and the Crimean Peninsula. To achieve the aim, the following issues were solved:

1) to analyze the annual variation in mineral phosphorus concentrations in both the water column and brown algae *Cystoseira crinita* and *Cystoseira barbata* in the inner part of the Streletskaya Bay based on monthly monitoring of 09.04.2023–31.03.2024;
2) to identify the mechanisms regulating mineral phosphorus accumulation in the studied *Cystoseira* species in relation to its varying concentrations in algae and water;
3) to assess the vertical biomass distribution of *Ericaria* sp. *crinita* (Duby) Molinari & Guiry and *Gongolaria barbata* (Stackhouse) Kuntze in waters of SPNAs, the Sevastopol Bay, and the Crimean Peninsula;
4) to quantify mineral phosphorus pools in macrophytobenthos and evaluate its functions in extracting biogenic elements from the dissolved phase of the aquatic environment and acting as a biochemical barrier to water hypereutrophication.

MATERIAL AND METHODS

Material was sampled during hydrobiological surveys in the Streletskaya Bay (44.59597108177086°, 33.46977409556002°) in 2023–2024 and off the Southwestern Crimea (Sevastopol region) in 2015–2024 (Fig. 1).

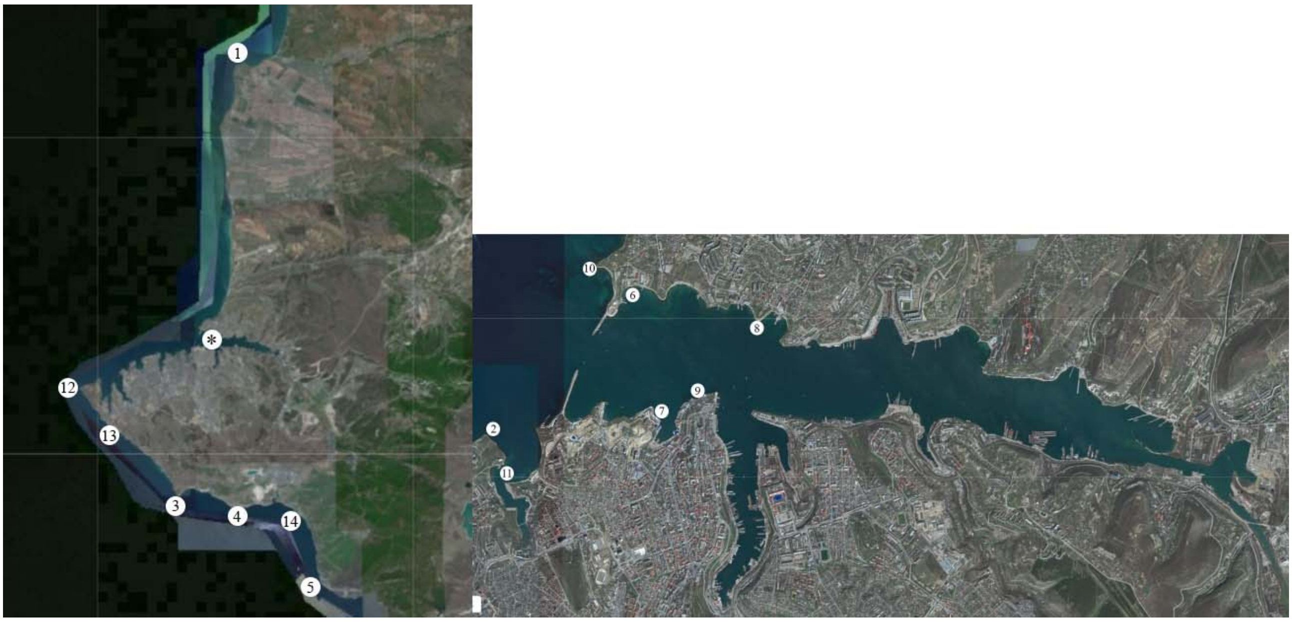

Fig. 1. Map of the location of sampling stations for the study of macrophytobenthos in the coastal zone of the Southwestern Crimea (Sevastopol region) in 2015–2021: 1, natural monument Coastal Aquatic Complex near Cape Lukull; 2, natural monument Coastal Aquatic Complex near the Chersonesus Nature Reserve; 3, natural monument Coastal Aquatic Complex near the Cape Fiolent; 4, state natural landscape reserve Karansky; 5, state natural landscape reserve Cape Aya; 6, the Konstantinovskaya Bay; 7, the Cape Khrustalny; 8, the Cape Kordon; 9, water area near the Monument to the Sunken Ships; 10, the Cape Severnaya Kosa; 11, the Karantinnaya Bay, an entrance Cape Vostochny; 12, the Cape Chersonesus; 13, the Golubaya Bay; 14, water area off the Seraya Rock (near Balaklava); 15, the Streletskaya Bay; *, stations within the Sevastopol Bay

Brown algae were sampled at depths of 1.0–1.5 m, with water temperature measured at 0.3 m using a Lowrance Hook-5 fishfinder equipped with a GPS navigator. Tidal and seiche variations in bay waters were recorded (those did not exceed 0.2–0.4 m), along with meteorological conditions. When the wind speeds exceeded 8 $m \cdot s^{-1}$ or there was precipitation, sampling was not carried out. As known [AlgaeBase, 2024], brown algae *Cystoseira crinita* and *Cystoseira barbata* have been reclassified: now, these ones are *Ericaria* sp. *crinita* and *Gongolaria* sp. *barbata*, respectively. No genus-specific differences in phosphorus metabolism were recorded for these algae. In tables with processed data and figures with mineral phosphorus concentrations, algae were reported exclusively as *Ericaria crinita*. It was assumed that variability from unaccounted hydrodynamic, meteorological, hydrochemical, and biological factors fell within the confidence intervals of parameter distributions; those were determined at a significance level of $\alpha = 0.05$.

To analyze the composition and structure of the macrophytobenthos and the *Ericaria*-dominated phytocenosis, *Ericaria crinita* + *Gongolaria barbata* – *Cladostephus spongiosus* – *Ellisolandia elongata*, and to investigate the biomass distribution of dominant and associated species, we used hydrobotanical survey data (Fig. 1) obtained during summer in the coastal zone (Fig. 2) of the Southwestern Crimea (Sevastopol region). Survey transects were laid in sites with differing land-use types: in waters within SPNAs of Sevastopol and in spots adjacent to shipping lanes and recreational areas.

Fig. 2. Biotope of *Ericaria crinita* and *Gongolaria barbata* in the coastal zone of the Southwestern Crimea (the Cape Fiolent, depth of 1 m, photo by S. Raksha)

Quantitively, macrophytobenthos was sampled along 12 hydrobotanical transects following a standardized hydrobotanical method [Kalugina-Gutnik, 1975]. At each depth (0.5, 1, 3, 5, and 10 m), a 25 × 25 cm recording frame was laid in four replicates deployed by scuba divers from the small research vessel "Viktoriya" (IBSS). For each station, the following parameters were recorded: total projective cover (%), type of bottom sediments, and condition of benthic phytocenoses and key species populations. A total of 268 quantitative macrophytobenthic samples were processed.

Methods of macrophytobenthic sample processing. Macrophytes were rinsed with flowing seawater to remove impurities: benthic sediments and epiphytic organisms. For each sample, we established wet weight (> 0.1 g) of lithophytic species and their epiphytic synusiae, total phytomass of macrophytes (g), and number of dominant species (ind.). For each depth stratum, species-specific biomass ($g \cdot m^{-2}$) and abundance ($ind. \cdot m^{-2}$) were calculated to characterize macrophytobenthic community development and the specificity of its spatial distribution.

Macroalgae were identified in accordance with monographic references [Vinogradova, 1974; Zinova, 1967] considering updates: taxonomic revisions and nomenclatural changes [AlgaeBase, 2024]. When describing the macrophytobenthos structure, we used the classification of the Black Sea benthic vegetation established by A. Kalugina-Gutnik [1975].

Methods for hydrochemical water analysis and macroalgal chemical composition determination. For chemical analysis, we selected apical thallus branches of algae [Kompleksnaya adaptatsiya, 1985] which showed the highest physiological activity based on results of algological assessments and ^{32}P experiments [Popovichev, Egorov, 2009]. Sample preparation followed standard methods [GOST 26263-84, 1985], while mineral phosphorus content was determined according to [Metody, 1988]. Mineral phosphorus concentrations in both water and algal samples were measured in triplicate. Analyzed algal fragments consisted of the 3rd to 4th order branches. For phosphorus quantification, a 0.1 g of aliquot (prewashed, dried, and ground) was ashed in a muffle furnace at +750 °C until converted to light grey powder. An ashed sample was dissolved in 1 mL of concentrated hydrochloric acid and diluted to 100 mL with distilled water. Subsequent analysis involved the phosphomolybdenum complex and its further restoration to an intensely blue compound with maximum wave absorbance at 885 nm (Murphy–Riley method). The wet-to-dry biomass conversion factor, k, was 4.11.

Computational and statistical data processing methods. Obtained results were analyzed using ratios derived from the theory of radioisotope and chemical homeostasis of marine ecosystems [Egorov, 2021; Polikarpov, 1964]. The phosphorus accumulation factor (K_n) in *E. crinita* thalli was calculated by the following formula accounting for parameter dimensionality:

$$K_n = 1,000 \times C_{erc}/C_w \,, \tag{1}$$

where C_{erc} and C_w are concentrations of mineral phosphorus in algae ($mg \cdot kg^{-1}$ wet weight) and in water ($\mu g \cdot L^{-1}$), respectively.

Based on observational data, the relationships between parameters of the power function (C_{erc} and K_n) and the independent variable (C_w) were determined by equations:

$$C_{erc} = {C_w}^{b}$$

or

$$K_n = {C_w}^{b1} \,, \tag{2}$$

where b and b1 are indicators of degree representing process rates.

The mineral phosphorus pool (in %) in benthic phytocenoses (P_{alg}) relative to its content in aquatic environment (P_w) was estimated as follows:

$$\mathrm{P}_{alg}(\%) = 100 \times (1 + 1/(m_{\mathrm{sp}}1,000(C_{alg}/C_w))) \tag{3}$$

and

$$\mathrm{P}_{alg}(\%) = 100 \times (1 + 1/(m_{\mathrm{sp}}K_n/10^6 h))\,, \tag{4}$$

where m_{sp} is *E. crinita* biomass (g·m^{-2} wet weight);

h is algal growth depth (m).

Data were statistically processed in Statistica 12; the standard deviation (σ) and the coefficient of determination (R^2) were calculated for hydrochemical and phytocenotic parameters. The statistical significance of regression coefficients and the linearity of dependencies were assessed using Student's *t*-test [Parchevskaya, 1969].

RESULTS AND DISCUSSION

Monitoring data on the mineral phosphorus content in surface waters and in *E. crinita* obtained from the estuarine zone of the Streletskaya Bay are detailed in Table 1.

Table 1. Results of determination of nutrient concentration in water and a brown alga *Ericaria crinita* in the Streletskaya Bay

Date	Day number of the year	Water temperature (°C)	H_2PO_4 concentration in water ± σ (µg P·L^{-1})	Phosphorus concentration in *E. crinita* ± σ (mg·kg^{-1} wet weight)	Phosphorus accumulation factor (K_n) in *E. crinita* (*per* wet weight)
09.04.2023	99	+13.2	3.8 ± 0.10	377.1 ± 45	99,244
28.05.2023	149	+16.0	9.0 ± 0.14	194.6 ± 23	21,627
24.06.2023	174	+20.0	7.0 ± 0.11	184.9 ± 22	26,416
24.07.2023	206	+25.3	10.5 ± 0.16	187.3 ± 22	17,872
23.08.2023	236	+25.6	6.0 ± 0.09	197.0 ± 24	32,846
14.09.2023	258	+25.3	7.0 ± 0.11	192.2 ± 23	27,459
20.10.2023	294	+23.4	6.4 ± 0.11	219.0 ± 26	34,215
22.11.2023	316	+14.1	7.0 ± 0.11	238.4 ± 29	34,063
25.12.2023	360	+11.3	7.0 ± 0.11	235.0 ± 28	35,576
18.01.2024	18	+8.8	4.0 ± 0.06	253.0 ± 30	63,260
28.02.2024	57	+9.6	14.0 ± 0.21	248.0 ± 30	17,714
31.03.2024	91	+12.5	11.0 ± 0.17	170.0 ± 20	15,454
Mean			7.7 ± 2.90	224.7 ± 27	35,300 ± 27,800

Note: σ, standard deviation.

The results of monitoring (Table 1) revealed weakly pronounced decreasing tendencies in mineral phosphorus concentrations within a year both in surface waters and in *E. crinita* from the Streletskaya Bay (see Fig. 3B, C). H_2PO_4 content in water ranged 3.8 to 14.0 µg·L^{-1}; mean values of C_w

were of (7.7 ± 2.9) $\mu g \cdot L^{-1}$. In *E. crinita*, concentrations varied within 170.0–377.1 $mg \cdot kg^{-1}$ wet weight, and C_{erc} averaged (224.7 ± 55.3) $mg \cdot kg^{-1}$. The phosphorus accumulation factor for this alga ranged 15,454 to 99,244; mean K_n values were of (35,300 ± 27,800).

Comparative analysis of development of macrophytobenthos and accompanying species showed as follows: regardless of location, the *Ericaria*-dominated phytocenosis reached maximum biomass values at depths of 0.5–1 m, particularly in open coastal waters (Tables 2, 3). *E. crinita* and *G. barbata* contribution to total phytocenosis biomass consistently decreased with depth, namely 1.5-fold in zones of SPNAs and coastal waters and 4.3-fold in the Sevastopol Bay (Table 3). Importantly, with a drop in *E. crinita* and *G. barbata* contribution to the total phytocenosis biomass, the role of accompanying species increased, including epiphytic synusiae. This indicated a shift in growing conditions, irradiance, water transparency, and the composition of bottom sediments. Furthermore, the combined effect of these factors largely determined the structural features and development of the macrophytobenthos in the studied areas. The greatest increase in the contribution of accompanying species with depth was recorded within a range of 5 to 10 m, especially in the areas of the Sevastopol Bay and its inner part (Table 3), where this indicator reached 61.2–95.2%.

Table 2. Changes in biomass ($g \cdot m^{-2}$) of the *Ericaria*-dominated phytocenosis by depth in various areas of the coastal zone of Sevastopol (the Southwestern Crimea, 2015–2021)

Polygon	Biomass at different depths				
	0.5 m	1 m	3 m	5 m	10 m
Coastal zones of SPNAs (polygon 1)					
Natural monument Coastal Aquatic Complex near Cape Lukull	754	4,751	3,635	3,556	3,134
Natural monument Coastal Aquatic Complex near the Chersonesus Nature Reserve	1,780	2,627	3,904	2,310	751
Natural monument Coastal Aquatic Complex near the Cape Fiolent	4,445	3,480	1,892	4,461	1,995
State natural landscape reserve Karansky	6,471	8,475	4,382	3,739	1,307
State natural landscape reserve Cape Aya	5,819	3,352	1,953	4,716	3,432
The Sevastopol Bay (polygon 2)					
The Konstantinovskaya Bay, entrance cape	992	423	424	35	–
The Cape Khrustalny	745	1,224	1,310	306	13
The Cape Kordon	4,700	5,064	2,323	1.2	–
Water area near the Monument to the Sunken Ships	5,483	3,416	1,864	655	–
Open coastal waters (polygon 3)					
The Cape Severnaya Kosa	11,458	12,889	5,572	3,157	131
The Karantinnaya Bay, an entrance Cape Vostochny	7,035	5,286	4,450	1,621	702
The Cape Chersonesus	7,727	11,755	14,068	9,045	2,391
The Golubaya Bay	5,224	3,817	3,039	5,741	4,906
Water area off the Seraya Rock	8,000	5,465	8,376	3,839	3,945

Table 3. Change in biomass (g·m^{-2}) of *Ericaria crinita*, *Gongolaria barbata*, and associated species, as well as change in their contribution (%) to biomass of the *Ericaria*-dominated phytocenosis, by depth in the coastal zone of Sevastopol (2015–2021)

Polygon	Biomass and contribution at different depths				
	0.5 m	1 m	3 m	5 m	10 m
Coastal zones of SPNAs (polygon 1)					
Natural monument Coastal Aquatic Complex near Cape Lukull	653 (86.6) 101 (13.4)	4,588 (96.6) 163 (3.4)	2,751 (75.7) 884 (24.3)	2,544 (71.5) 1,012 (28.5)	2,600 (83) 534 (17)
Natural monument Coastal Aquatic Complex near the Chersonesus Nature Reserve	1,629 (91.5) 151 (8.5)	2,369 (90.2) 260 (9.8)	2,813 (72.1) 1,091 (27.9)	1,335 (57.8) 975 (42.2)	292 (38.9) 459 (61.1)
Natural monument Coastal Aquatic Complex near the Cape Fiolent	4,324 (97.3) 121 (2.7)	3,220 (92.5) 260 (7.5)	1,266 (66.9) 626 (33.1)	2,909 (65.2) 1,552 (34.8)	1,376 (69) 619 (31)
State natural landscape reserve Karansky	5,621 (86.9) 850 (13.1)	7,603 (89.7) 872 (10.3)	3,440 (78.6) 942 (21.4)	2,603 (66.6) 1,136 (33.4)	716 (54.8) 591 (45.2)
State natural landscape reserve Cape Aya	5,016 (86.2) 803 (13.8)	3,025 (90.2) 327 (9.8)	1,666 (85.3) 287 (14.7)	3,912 (83) 804 (17)	1,537 (44.8) 1,895 (55.2)
The Sevastopol Bay (polygon 2)					
The Konstantinovskaya Bay, entrance cape	623 (62.8) 369 (37,2)	310 (73.4) 113 (26.6)	185 (43.6) 239 (56.4)	3 (9.3) 32 (90.7)	–
The Cape Khrustalny	522 (70.1) 223 (29.9)	980 (80.1) 244 (19.9)	588 (44.9) 722 (55.1)	168 (54.7) 138 (45.3)	9 (71.7) 4 (28.3)
The Cape Kordon	4,060 (86.4) 640 (13.6)	4,415 (87.2) 649 (12.8)	1,823 (78.5) 500 (21.5)	no *Cystoseira*	–
Water area near the Monument to the Sunken Ships	4,766 (86.9) 717 (13.1)	2,894 (84.7) 522 (15.3)	727 (39.0) 1,137 (61.0)	212 (32.4) 453 (67.6)	–
Open coastal waters off Sevastopol (polygon 3)					
The Cape Severnaya Kosa	10,765 (94.0) 693 (6.0)	12,314 (95.5) 575 (4.5)	4,333 (77.8) 1,239 (22.2)	2,042 (64.7) 1,115 (35.3)	7 (5.3) 124 (94.7)
The Karantinnaya Bay, an entrance Cape Vostochny	6,166 (87.7) 869 (12.3)	4,883 (92.4) 403 (7.6)	2,878 (64.7) 1,572 (35.3)	1,035 (63.8) 586 (36.2)	456 (65.1) 246 (34.9)
The Cape Chersonesus	6,713 (86.9) 1,014 (13.1)	10,658 (90.7) 1,097 (9.3)	11,197 (79.6) 2,871 (20.4)	6,157 (68.1) 2,888 (31.9)	1,789 (74.8) 602 (25.2)
The Golubaya Bay	4,384 (83.9) 840 (16.1)	2,798 (73.3) 1,019 (26.7)	2,301 (75.7) 738 (24.3)	3,496 (60.9) 2,245 (39.1)	4,243 (86.5) 663 (13.5)
Water area off the Seraya Rock	6,943 (86.8) 1,057 (13.2)	4,441 (81.3) 1,024 (18.7)	5,586 (66.7) 2,790 (33.3)	2,253 (58.7) 1,586 (41.3)	2,203 (55.8) 1,742 (44.2)

Note: in the numerator, the total biomass of *E. crinita* and *G. barbata* is provided, and in brackets, the proportion of these species (%) in the phytocenosis biomass is given. In the denominator, the biomass of associated species is provided, and in brackets, their contribution (%) to the phytocenosis biomass is given.

Based on mean values of the specific biomass of the phytocenosis (m_{sp}) across areas and depths, *E. crinita* and *G. barbata* contribution to it was assessed (Tables 2, 3). For these species, the mean m_{sp} values (converted to wet weight) at depths of 0.5, 1, 3, 5, and 10 m were as follows:

- in area 1, (3,853 ± 2,980), (4,537 ± 2,930), (3,153 ± 1,155), (3,756 ± 3,153), and (2,132 ± 1,151) g·m^{-2}, respectively;
- in area 2, (2,980 ± 2,461), (2,636 ± 2,280), (1,864 ± 816), (181 ± 316), and (6 ± 3) g·m^{-2};

- in area 3, (7,906 ± 2,305), (7,842 ± 4,158), (7,101 ± 4,359), (4,680 ± 2,353), and (2,445 ± 2,323) g·m^{-2}.

Contribution of *E. crinita* and *G. barbata* biomass to the specific biomass of the phytocenosis at depths of 0.5, 1, 3, 5, and 10 m was estimated as follows:

- in area 1, (89.7 ± 4.8), (81.8 ± 2.9), (75.7 ± 6.9), (68.8 ± 9.3), and (58.1 ± 18.0) %, respectively;
- in area 2, (76.5 ± 12.0), (81.3 ± 6.1), (51.5 ± 18.2), (25.0 ± 24.5), and (17.9 ± 35.8) %;
- in area 3, (87.9 ± 3.7), (86.6 ± 9.1), (72.9 ± 6.7), (63.2 ± 3.6), and (57.4 ± 31.5) %.

Involving the obtained data and applying equations (3) and (4), we established the contribution of the *Ericaria*-dominated phytocenosis to water de-eutrophication and the capacity of *E. crinita* and *G. barbata* to concentrate mineral phosphorus. The results of monthly measurements of the annual water temperature cycle and changes in the phosphorus concentration characteristics in water and in the brown algae from the inner part of the Streletskaya Bay are presented in Fig. 3.

The analysis of features of mineral phosphorus concentration in the brown algae (Fig. 3) revealed patterns related to its content in the aquatic environment. When examining the C_w and C_{alg} relationship in linear coordinates, the accumulation capacity of the brown algae was found to decrease with R^2 = 0.193. Student's *t*-test for the linear regression coefficient significance showed its calculated value, t_{obs} = 1.54, to be below the critical one, t_{cr} = 2.228, at the significance level of α = 0.05 (with $n - 2 = 10$ degrees of freedom). Consequently, the observed decreasing tendency in algal mineral phosphorus concentration with rising aquatic content was statistically insignificant.

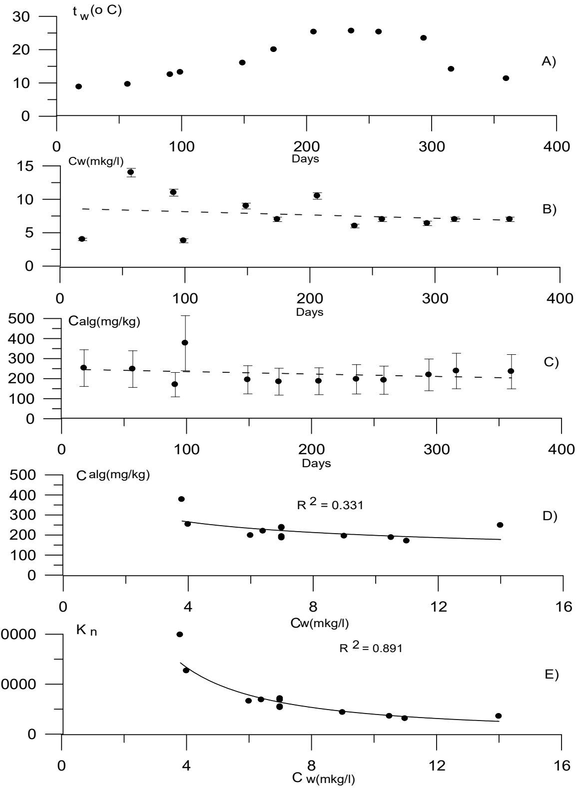

Fig. 3. Changes in temperature (A), concentration of mineral phosphorus in the surface layer of water (B) and in brown algae (C), and dependence of concentration (D) and accumulation coefficients (E) of mineral phosphorus by algae in the Streletskaya Bay (2023–2024)

The data plotted on double logarithmic axes, corresponding to a power-law dependence between C_w and C_{alg}, are presented in Fig. 3D. In this case, the correlation between mineral phosphorus concentrations in water and in *E. crinita* was characterized by a coefficient of determination $R^2 = 0.331$. For this function, the parameters of Student's *t*-test were as follows: the calculated value, t_{obs}, was 2.224, and its critical value, t_{cr}, was 1.812 (at $\alpha = 0.100$). These results were interpreted from the perspective of a type II error [Nalimov, 1971], *i. e.*, the probability of rejecting the hypothesis that a power function reliably describes the experimental observations. The analysis indicated as follows: in 90% of cases, the sample parameters of the power-law dependence between C_w and C_{alg} shown in Fig. 3D fell within the range of parameter scatter for the general population.

Data analysis on the change in the algae concentrating function, expressed *via* accumulation factors (K_n), showed that the relationship between C_w and K_n was described by a linear regression equation with $R^2 = 0.562$. This relationship corresponds to $t_{obs} = 3.567$ (higher than $t_{cr} = 2.228$). Accordingly, it can be considered significant at $\alpha = 0.05$. A comparison of the linearity index ($\xi = 0.439$) of this function with its error estimate ($O_\xi = 0.209$) demonstrated that the relationship between C_w and K_n is non-linear. However, it (see Fig. 3E) can be approximated by a power function with high statistical significance ($R^2 = 0.891$):

$$K_n = 417,000 C_w^{-1.321} . \tag{5}$$

This function was further applied to determine the mineral phosphorus pool in the algae.

Based on calculations by formula (4), the mineral phosphorus pools in the *Ericaria*-dominated phytocenosis and in *E. crinita* specifically were determined (Table 4). These values are presented relative to the total phosphorus content under 1 m^2 of the water column, incorporating the scatter of the accumulation factor values (Table 1).

Table 4. Changes in the mean proportion of mineral phosphorus pool (%) (the numerator) and its range (the denominator) in the biomass of the *Ericaria*-dominated phytocenosis by depth in the coastal zone of Sevastopol (2015–2021)

Polygon	Depth, m				
	0.5	1	3	5	10
1, coastal zones of SPNAs	99.5 99.2–99.9	99.9 99.6–99.8	96.1 94.2–99.1	95.6 92.1–98.7	86.1 76.7–95.5
2, the Sevastopol Bay	99.3 98.7–99.8	98.5 97.8–99.7	91.5 85.6–97.5	84.7 74.4–94.9	78.0 64.0–92.0
3, open coastal waters	99.8 99.5–99.9	99.5 99.2–99.9	98.5 97.4–99.6	96.7 93.6–99.9	77.1 78.9–96.0

Note: numbers and names of polygons correspond to those in Tables 2, 3.

The data presented in Table 4 evidence for the fact that the highest phosphorus pool values and its most pronounced decrease were observed in open coastal waters: 99.5% at a depth of 0.5 m and 77.1% at 10 m. The pool dropped in water areas from the upper to middle sublittoral zone (from 0.5 to 10 m). The data in Table 4 indicate as follows: in a depth range down to 10 m, the *Ericaria*-dominated phytocenosis can almost completely extract mineral phosphorus from the aquatic environment, thereby limiting its availability for other primary producers.

Nearly all macrophytic communities in the Crimea have coastal and dynamic boundaries. The content of biogenic elements in these areas is governed by both biogeochemical factors and external effects. *Via* biogeochemical processes, biogenic elements are extracted from dissolved state and concentrated in living and abiotic components of ecosystems thus acquiring densities differing from seawater's specific density and becoming incorporated into biogeochemical cycles which involve their turnover, coastal deposition, and elimination into aquatic and geological reservoirs. Experimental studies using radioactive ^{32}P labeling have shown that phosphorus exchange kinetics in *E. crinita* follows a compartmental model, according to which algal uptake of mineral phosphorus from water environment follows Michaelis–Menten equation [Patton, 1968], and its lifetime excretion is described by first-order metabolic reactions [Popovichev, Egorov, 2009]. *E. crinita* maintains phosphorus pools, dynamics of which depends on the volume–mass ratios of branches of different orders and which exchange at varying rates. Thus, the mean phosphorus exchange rate in this species was 0.16 day^{-1}, and the phosphorus turnover period was approximately 6 days.

The influx of biogenic elements *via* precipitation, slope runoff, and river discharge can alter chemical limitation characteristics in primary production processes [Egorov et al., 2023]. Advective processes and the Rim Current with velocity up to 1 $\mathrm{m \cdot s^{-1}}$ facilitate biogenic element exchange with adjacent areas and open waters [Egorov et al., 2018]. Macrobiocenoses function as open systems, where steady-state concentrations of dissolved biogenic elements are determined by the balance between input and elimination fluxes. This equilibrium results from the combined effect of all the accounted and unaccounted factors. In this context, effective application of biogeochemical criteria requires either assessment of dissolved nutrient thresholds leading to water hypereutrophication or development of regulatory standards for maximum permissible input fluxes, particularly in areas with high recreational or touristic value. It is known that power functions of the type (2) are widely used to describe biogeochemical interactions between biotic and abiotic components with radioactive and chemical substances of marine environment. When parameters b and b1 are positive, the power function corresponds to the Freundlich equation characterizing sorption saturation in solids. With negative values of b and b1, the equation (2) reflects concurrent sorption and metabolic processes. Asymptotic estimates of K_n and C_{alg} values calculated *via* equation (2) as functions of C_w enable prediction of water self-purification capacity limits [Egorov, 2021]. Therefore, the data presented in this study constitute a phase of research aimed at investigating the sequestration of mineral phosphorus by macrophytocenoses as a factor determining their role as a barrier to water de-eutrophication, and also a parametric database for utilizing biogeochemical criteria to regulate the maximum permissible flows of anthropogenic effect.

Conclusions:

1. At mineral phosphorus concentrations in water of 3.8–10.5 $\mathrm{\mu g \cdot L^{-1}}$, a brown alga *Ericaria crinita* accumulates it within a range of 170.0–377.1 $\mathrm{mg \cdot kg^{-1}}$ wet weight, with a mean value of (224.7 ± 55.7) $\mathrm{mg \cdot kg^{-1}}$; accumulation factor values range 15,454 to 92,244 units, with a mean of (35,300 ± 27,800). The concentrating capacity of perennial brown algae, expressed as K_n, decreases with rising mineral phosphorus content in the aquatic environment. This relationship follows a power function with a negative exponent indicating the rate of decrease. The strength of the dependence between the mineral phosphorus concentration in water C_w and the accumulation factor K_n is characterized by a high coefficient of determination: $R^2 = 0.891$. The probability of rejecting the hypothesis of a power-law relationship between the mineral phosphorus concentration in water and in algae is 90%.
2. The mineral phosphorus pool within the *Ericaria*-dominated phytocenosis dropped with depths 0.5 to 10.0 m in all investigated areas: in zones of specially protected natural areas, from 99.5 to 86.1%; in the Sevastopol Bay, from 99.3 to 78.0%; and in open coastal waters, from 96.8 to 77.1%. In general, this phytocenosis absorbs and retains over 80% of the mineral phosphorus occurring in the water column, while releasing back only up to 16% of maximum absorbed flux daily.
3. The perennial *Ericaria*-dominated phytocenosis that prevails off the Southwestern Crimea can extract mineral phosphorus almost completely from the aquatic environment, thereby limiting its availability for other producers. This study is the first to reveal its significant role in sequestering mineral phosphorus in the Black Sea waters off the coast of the Southwestern Crimea.
4. These results can be used to develop measures for improving coastal water quality in the context of intensifying natural resource use. Moreover, they can help in forecasting probable changes in coastal ecosystems under increasing anthropogenic load and other adverse factors, particularly those arising from the development of industrial, transport, recreational, and other zones along the Russian coast of the Black Sea.

This work was carried out within the framework of IBSS state research assignment "Study of biogeochemical patterns of radioecological and chemoecological processes in the ecosystems of water bodies of the Sea of Azov–Black Sea Basin in comparison with other areas of the World Ocean and individual aquatic ecosystems of their drainage basins to ensure sustainable development in the southern seas of Russia" (No. 124030100127-7) and "Biodiversity as the basis for the sustainable functioning of marine ecosystems, criteria and scientific principles for its conservation" (No. 124022400148-4).

REFERENCES

1. Aleksandrov B. G. *Gidrobiologicheskie osnovy upravleniya sostoyaniem pribrezhnykh ekosistem Chernogo morya.* Kyiv : Naukova dumka, 2008, 343 p. (in Russ.)
2. Vernadsky V. I. *Khimicheskoe stroenie biosfery Zemli i ee okruzheniya.* Moscow : Nauka, 1965, 374 p. (in Russ.)
3. Vinogradova K. L. *Ul'vovye vodorosli (Chlorophyta) morei SSSR.* Leningrad : Nauka, Leningr. otd-nie, 1974, 166 p. (in Russ.)
4. GOST 26263-84. *Pochvy. Metody opredeleniya valovogo fosfora i valovogo kaliya* : gosudarstvennyi standart Soyuza SSR : utverzhden i vveden v deistvie Postanovleniem Gosudarstvennogo komiteta SSSR po standartam ot 21.08.1984 No. 2939 : vveden vpervye : data vvedeniya 1985-07-01 / podgotovlen Ministerstvom sel'skogo khozyaistva SSSR. Moscow : Izdatel'stvo standartov, 1985, 11 p. (in Russ.)
5. Gubanov V. I., Mal'chenko Yu. A., Kuftarkova E. A., Kovrigina N. P. Diagnosis of modern state of coastal water near Sevastopol (the Black Sea) according to monitoring of chemical parameters. *Ekologicheskaya bezopasnost' pribrezhnoi i shel'fovoi zon i kompleksnoe ispol'zovanie resursov shel'fa*, 2004, iss. 10, pp. 141–148. (in Russ.). https://elibrary.ru/ymtpgd
6. Egorov V. N. *Theory of Radioisotope and Chemical Homeostasis of Marine Ecosystems.* Sevastopol : IBSS, 2019, 356 p. (in Russ.). https://doi.org/10.21072/978-5-6042938-5-0
7. Egorov V. N., Plugatar Yu. V., Malakhova L. V., Mirzoeva N. Yu., Gulin S. B., Popovichev V. N., Sadogurskii S. E., Malakhova T. V., Shchurov S. V., Proskurnin V. Yu., Bobko N. I., Marchenko Yu. G., Stetsyuk A. P. Ekologicheskoe sostoyanie akvatorii osobo okhranyaemoi prirodnoi territorii "Mys Mart'yan" i problema realizatsii ee ustoichivogo razvitiya po faktoram evtrofikatsii, radioaktivnogo i khimicheskogo zagryazneniya vod. In: *Sokhranenie biologicheskogo raznoobraziya i zapovednoe delo v Krymu* : materialy nauchno-prakticheskoi konferentsii s mezhdunarodnym uchastiem, Yalta, 23–26 oktyabrya 2018 g. Yalta, 2018, pp. 36–40. (Nauchnye zapiski prirodnogo zapovednika "Mys Mart'yan" ; iss. 9). (in Russ.). https://doi.org/10.25684/NBG.scnote.009.2018.04
8. Egorov V. N., Mirzoyeva N. Yu., Artemov Yu. G., Proskurnin V. Yu., Stetsiuk A. P., Marchenko Yu. G., Evtushenko D. B., Moseichenko I. N., Chuzhikova-Proskurnina O. D. The possibility of implementation of the sustainable development concept for the recreational coastline of Yalta city regarding biogenic elements, radionuclides, heavy metals, and organochlorine compounds (Crimea, Black Sea). *Marine Biological Journal*, 2023, vol. 8, no. 3, pp. 12–32. https://elibrary.ru/yhovfn
9. Zaitsev Yu. P., Garkavaya G. P., Nesterova D. A., Polishchuk L. N. The Danube as a basic source of the Black Sea

eutrophication. *Gidrobiologicheskii zhurnal*, 1989, vol. 25, no. 4, pp. 21–23. (in Russ.)

10. Zilov E. A. *Gidrobiologiya i vodnaya ekologiya (organizatsiya, funktsionirovanie i zagryaznenie vodnykh ekosistem)*. Irkutsk : Izd-vo Irkutskogo gos. un-ta, 2009, 147 p. (in Russ.). https://elibrary.ru/qkspbj
11. Zinova A. D. *Opredelitel' zelenykh, burykh i krasnykh vodoroslei yuzhnykh morei SSSR*. Moscow ; Leningrad : Nauka, 1967, 400 p. (in Russ.)
12. Ivanov V. A., Ovsyany E. I., Repetin L. N., Romanov A. S., Ignatyeva O. G. *Hydrological and Hydrochemical Regime of the Sebastopol Bay and Its Changing Under Influence of Climatic and Anthropogenic Factors* / NAS of Ukraine, Marine Hydrophysical Institute. Sevastopol, 2006, 90 p. (in Russ.). https://elibrary.ru/yriouu
13. Izrael Iu. A., Tsyban A. V. On the assimilation capacity of the World Ocean. *Doklady Akademii nauk SSSR*, 1983, vol. 272, no. 3, pp. 702–704. (in Russ.)
14. Kalugina-Gutnik A. A. *Fitobentos Chernogo morya*. Kyiv : Naukova dumka, 1975, 248 p. (in Russ.). https://repository.marine-research.ru/handle/299011/5645
15. *Kompleksnaya adaptatsiya tsistoziry k gradientnym usloviyam: nauchnye i prikladnye problemy* / S. A. Kovardakov, A. V. Prazukin, Yu. K. Firsov, A. E. Popov. Kyiv : Naukova dumka, 1985, 216 p. (in Russ.). https://repository.marine-research.ru/handle/299011/8319
16. *Red Book of the Republic of Crimea. Plants, Algae, and Fungi* / A. V. Yena, A. V. Fateryga (Eds). Simferopol : ARIAL, 2015, 480 p. (in Russ.). https://elibrary.ru/wxeqef
17. Kuftarkova E. A., Gubanov V. I., Kovrigina N. P., Eremin I. Yu., Senicheva M. I. Ecological assessment of modern state of waters in the region of interaction of the Sevastopol Bay and part of the sea contiguous to it. *Morskoj ekologicheskij zhurnal*, 2006, vol. 5, no. 1, pp. 72–91. (in Russ.). https://repository.marine-research.ru/handle/299011/851
18. *Metody gidrokhimicheskikh issledovanii osnovnykh biogennykh elementov*. Moscow : VNIRO, 1988, 119 p. (in Russ.)
19. *Marine Protected Areas of the Crimea. Scientific Handbook* / N. A. Milchakova, V. V. Aleksandrov, L. V. Bondareva, T. V. Pankeeva, E. B. Chernysheva / N. A. Milchakova (Ed.). Simferopol : N.Orianda, 2015, 312 p. (in Russ.). https://repository.marine-research.ru/handle/299011/1399
20. Nalimov V. V. *Teoriya eksperimenta*. Moscow : Nauka, 1971, 207 p. (in Russ.). https://elibrary.ru/rxymdy
21. Patton A. R. *Biochemical Energetics and Kinetics* : transl. from Engl. by Z. F. Bogautdinov. Moscow : Mir, 1968, 159 p. (in Russ.)
22. Parchevskaya D. S. *Statistika dlya radioekologov (prakticheskoe rukovodstvo po statistike i planirovaniyu eksperimentov v radioekologii)*. Kyiv : Naukova dumka, 1969, 114 p. (in Russ.). https://repository.marine-research.ru/handle/299011/1109
23. Polikarpov G. G. *Radioekologiya morskikh organizmov*. Moscow : Atomizdat, 1964, 295 p. (in Russ.). https://repository.marine-research.ru/handle/299011/12748
24. Polikarpov G. G., Egorov V. M. Zdatnist' mors'kykh ekosystem do vydalennya radioaktyvnykh i khimichnykh zabrudnen' z fotychnogo sharu. *Visnyk AN URSR*, 1981, no. 2, pp. 73–81. (in Ukr.). https://repository.marine-research.ru/handle/299011/11224
25. Polikarpov G. G., Egorov V. N. *Morskaya dinamicheskaya radiokhemoekologiya*. Moscow : Energoatomizdat, 1986, 176 p. (in Russ.). https://repository.marine-research.ru/handle/299011/7683

26. Popovichev V. N., Egorov V. N. Kinetic regularities of exchange of phosphorus by the Black Sea brown seaweed *Cystoseira barbata*. *Morskoj ekologicheskij zhurnal*, 2009, vol. 8, no. 1, pp. 55–66. (in Russ.). https://repository.marine-research.ru/handle/299011/1000
27. Yunev O. A., Konovalov S. K., Velikova V. *Anthropogenic Eutrophication in the Black Sea Pelagic Zone: Long-term Trends, Mechanisms, Consequences* / A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS ; Marine Hydrophysical Institute of RAS. Moscow : GEOS, 2019, 164 p. (in Russ.). https://repository.marine-research.ru/handle/299011/7989
28. Egorov V. N. *Theory of Radioisotopic and Chemical Homeostasis of Marine Ecosystems.* Cham, Switzerland : Springer, 2021, 320 p. https://doi.org/10.1007/978-3-030-80579-1
29. Fiori E., Zavatarelli M., Pinardi N., Mazziotti C., Ferrari C. R. Observed and simulated trophic index (TRIX) values for the Adriatic Sea basin. *Natural Hazards and Earth System Sciences*, 2016, vol. 16, iss. 9, pp. 2043–2054. https://doi.org/10.5194/nhess-16-2043-2016
30. *AlgaeBase.* World-wide electronic publication, National University of Ireland, Galway / M. D. Guiry, G. M. Guiry (Eds) : [site], 2024. URL: http://www.algaebase.org [accessed: 09.10.2024].
31. Mee L. D. The Black Sea in crisis: A need for concerted international action. *Ambio*, 1992, vol. 21, pp. 278–286.
32. Oguz T., Gilbert D. Abrupt transitions of the top-down controlled Black Sea pelagic ecosystem during 1960–2000: Evidence for regime-shifts under strong fishery exploitation and nutrient enrichment modulated by climate-induced variations. *Deep Sea Research Part I: Oceanographic Research Papers*, 2007, vol. 54, iss. 2, pp. 220–242. https://doi.org/10.1016/j.dsr.2006.09.010
33. Redfield A. C. The biological control of chemical factors in the environment. *American Scientist*, 1958, vol. 46, no. 3, pp. 205–221.
34. Slepchuk K. A., Khmara T. V., Man’kovskaya E. V. Comparative assessment of the trophic level of the Sevastopol and Yuzhnaya bays using E-TRIX index. *Physical Oceanography*, 2017, no. 5, pp. 60–70. http://doi.org/10.22449/1573-160X-2017-5-60-70

МАКРОФИТОЦЕНОЗЫ КАК БИОГЕОХИМИЧЕСКИЕ БАРЬЕРЫ ГИПЕРЭВТРОФИКАЦИИ ВОД МИНЕРАЛЬНЫМ ФОСФОРОМ В АКВАТОРИЯХ ЮГО-ЗАПАДНОГО КРЫМА

В. Н. Егоров, Н. А. Мильчакова, Н. И. Бобко, Ю. Г. Марченко

ФГБУН ФИЦ «Институт биологии южных морей имени А. О. Ковалевского РАН»,
Севастополь, Российская Федерация
E-mail: *egorov@ibss-ras.ru*

Цель работы заключалась в изучении особенностей концентрирования минерального фосфора занесёнными в Красную книгу Республики Крым бурыми водорослями *Cystoseira crinita* и *Cystoseira barbata* и в оценке роли макрофитобентоса прибрежной экосистемы Юго-Западного Крыма в создании биогеохимических барьеров, регулирующих конкурентные отношения продуцентов за биогенные элементы. Определено, что *Cystoseira crinita* и *Cystoseira barbata* концентрируют минеральный фосфор до уровней 170,0–377,1 мг·кг$^{-1}$, в среднем (224,7 ± 55,7) мг·кг$^{-1}$ сырой массы, с коэффициентами накопления 15 454–92 244 единицы, в среднем (35 300 ± 27 800).

По новой номенклатуре семейства Sargassaceae Kützing, эти виды водорослей входят в состав эрикариевого фитоценоза *Ericaria crinita* + *Gongolaria barbata* – *Cladostephus spongiosus* – *Ellisolandia elongata* (*Ericaria* sp.). В целом бурые водоросли прибрежных биотопов поглощают и задерживают свыше 80 % объёма минеральных форм фосфора, содержащихся в водной среде, и ежедневно возвращают в неё лишь до 16 % его максимально поглощаемого потока, что является значимым фактором кондиционирования биогенного состава вод.

Ключевые слова: биогенные элементы, макрофитобентос, пул минерального фосфора в воде и водорослях, Юго-Западный Крым, Чёрное море