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STUDY OF PHOTOSYNTHETIC PIGMENTS IN THE HYPERHALINE KUYALNIK ESTUARY AND ITS INFLOWS (UKRAINE, NORTH-WESTERN BLACK SEA REGION)

Purpose. To investigate the interannual and intraannual analysis of the content of chlorophyll "a", "b", "c" and pheophytin in the Kuyalnik estuary (KE) and its tides for the period 2008-2012, to evaluate the spatial distribution of chlorophyll "a" in the water area of the estuary in different seasons year and reveal the connection of the specified characteristics with the abiotic factors of the environment.

Methods. Hydrochemical, biological and static analyses. The original geo-informational database of comprehensive monitoring of the KE basin was used.

Results. According to the results of generalization, analysis and systematization of the experimental studies materials of the photosynthetic pigments content (chlorophylls 'a', 'b', 'c') and pheophytin (the primary product of chlorophyll decomposition) in the surface waters of the hyperhaline Kuyalnik Estuary (KE) and its main water inflows (Velykyi Kuyalnyk river, drainage channels from the Peresyp and Korsuntsivsky ponds) during the period of low water content in the estuary (2008-2012) the interannual and intraannual distribution of pigment content is presented, their ratio in the specified water bodies and the spatial distribution of chlorophyll "a" content in the water area of KE in different seasons of the year are evaluated. It has been revealed that in the periods of low water content in KE and high salinization of its waters production activity is insignificant, but it does not stop. Adaptive mechanisms of algal communities in relation to extreme conditions of KE (salinization, decreasing of water level and increase of water temperature, decreasing of freshwater inflow) are expressed in an increase in the share of auxiliary pigments (chlorophylls "b" and "c"). The obtained ratios of pigments indicate mainly the dominance of diatom algae in all water bodies of the basin during the research period. A correlation analysis of the relationships between the concentrations of chlorophylls "a", "b", "c", concentrations of different chlorophylls and pheophytin and between chlorophyll "a" and the main abiotic factors of the environment (temperature, pH, dissolved oxygen in water, BOD₅, COD, ammonium nitrogen and phosphorus phosphate) were carried out.

Conclusions. The results of the study of the pigment fund CI indicate that the characteristics of the content of photosynthetic pigments and their ratio can be used as integral characteristics of the productivity and ecological state of water bodies.

KEY WORDS: *chlorophylls "a", "b", "c", pheophytin, ratio, Kuyalnyk Estuary, inflows, abiotic factor, interannual dynamics, intraannual dynamics, spatial distribution*

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Introduction

An important problem of the XXI century is the global warming and, as a result, salinization and drying of water bodies, salinization and desertification of territories, as a result of which there is a serious threat of biodiversity reducing [1-5]. As the consequence is the increasing of the relevance of studying the issues of plant resistance to extreme environmental factors.

The concentrations and ratios of plant pigments, in particular chlorophyll "a", as the main green photosynthetic pigment in the aquatic environment (phytoplankton, seston) and auxiliary light-harvesting pigments (chlorophylls "b" and "c") are important integral characteristics of the quantitative development and physiological state of algoflora communities, their systematic affiliation, reflect the capacity for production opportunities, allow to judge the degree of trophicity and the ecological state of water bodies [6-18]. The presence of chlorophyll "b" determines the development of small flagellated green algae, the massive development of blue-green algae was due to the increased content of chlorophyll "a" [16, 18].

In general, the ratio of chlorophyll "a" to chlorophyll "b" is an important indicator that characterizes the relationship between the plant and the environment [16-18]. It is important to

consider that the level and ratio of pigments can be influenced by both abiotic and biotic factors. Data on pheophytin content play an important role in characterizing the physiological state too. The ratio of the chlorophyll "a" content to the content of pheophytin ($Ca/Cph < 1$) indicates the death and decomposition of algae [16, 18, 19].

Actually, data on the chlorophyll "a" concentration in the water of the hyperhaline Kuyalnik Estuary (KE) are extremely limited [19], and information on the pigments content in its main inflows (Velykyi Kuyalnyk river, Peresypski and Korsuntsivski ponds [20]) was not available in the literature.

In this regard, this work presents a spatial-temporal analysis of the photosynthetic pigments (chlorophylls "a", "b", "c") content and the primary product of chlorophyll decomposition – pheophytin in the KE and its inflows in the period 2008-2012, and based on the results of monitoring materials summarizing of the KE ecosystem, an analysis of the relationship between the specified characteristics and the interdependence of the chlorophyll "a" content, on one hand, and the main hydrological and hydrochemical characteristics, on the other hand, was carried out.

Materials and methods

The analysis was carried out on the basis of original materials collected during 2008-2012 years in the water of the KE at stations of permanent integrated monitoring in the southern part of the water area – lower reaches (stations of observations 5, 6k, 8, 9k), the central part (stations 3, 4, 12, 13) and the northern part of the estuary - the upper part (st. 14) and in the main inflows - the Velykyi Kuyalnyk river, Peresypski (st. 9) and Korsuntsivski (st. 6) ponds.

The map-scheme of the observation stations of photosynthetic pigments in the surface waters location in the KE basin is presented on Fig. 1.

The coordinates of the observation stations were determined using GPS navigator.

The content of phytoplankton algae pigments was determined by a standard spectro-

photometric method [21] using spectrophotometer ULAB 102.

Water for hydrochemical analysis and determination of pigment content was collected in plastic bottles usually at a distance of 1,5-50 m from the shore at a depth 0,2-0,5 m.

Hydrochemical analysis and determination of pigments (chlorophyll "a", chlorophyll "b", chlorophyll "c" and pheophytin) were carried out in the "Monitoring" testing laboratory of the Physical-Chemical Institute of the Environment and Human Protection of the Ministry of Education and Science of Ukraine and the National Academy of Sciences of Ukraine (the laboratory is certified for the right to conduct measurements in the field of distribution of state metrological supervision; St. No.: 504/2007

dated 04/13/2007, RO-409/2010 dated 07/12/2010, RO-066/2014 dated 04/14/2014).

Water temperature was measured using a TL-4 glass thermometer with the scale of 0,1°C, pH – using a self-powered pH meter pH-150 MI at the time of sampling.

In total, during the research period 49 samples were taken and analyzed for the content of photosynthetic pigments in the surface waters of the estuary basin – 36 in the KE and 13 in its inflows.

Simultaneously with pigments concentration measurements the hydrochemical indicators (temperature, pH, salinity, dissolved oxygen, BOD₅, COD, ammonium nitrogen, phosphate

phosphorus) were measured in all named water bodies.

To study the relationship between the specified parameters a correlation analysis (r) according to Pearson was performed with a significance of $P = 0,05$.

The content of chlorophylls "a", "b", "c" in the specified water bodies of the KE basin in the period 2008-2012 years was determined mainly during the vegetation season from April to November. In February and April 2009 and November 2010 pheophytin was also determined at observation stations 5, 8, and 12 in the KE water area.



Fig. 1 – Location of photosynthetic pigments monitoring stations in the water area of the Kuyalnyk Estuary and its water inflows.

(based on the vector map of Odesa region M 1:50 000, CJSC “ECOMM Co”)

Results and discussion

A feature of hyperhaline KE is the significant variability of the water regime. It is charac-

terized by quick fluctuations in water level and salinity. That was during the period of photosyn-

thetic pigments research in the summer-autumn period of 2008-2012 the absolute values of water salinity at photosynthetic pigments monitoring stations ranged from 194 to 373‰, the average annual – in the range of 222-289‰.

At the same time, in the first decade of the XXI century a decrease in the morphometric indicators of the KE was recorded - twice on the water surface area. Also it was observed an almost tenfold reduction of channel runoff (river runoff – Velykyi Kuyalnyk, Doldoka, Kubanka rivers, "pond runoff" – the inflow from the Peresypski and Korsuntsivsky ponds) and the switching mainly to the type of water nutrition due to atmospheric precipitation [20]. Moreover, in May–September 2014 the water salinity varied within extremely narrow limits – 303–323‰. In order to stop the large-scale degradation processes of the KE ecosystem, it was made decision to fulfill the estuary with sea water starting from December 2014, in the winter-spring period. Sea water was supplied from the Odesa Bay through the pipeline to the southern part of estuary (about 10 million m³ annually).

The transportation of sea water from the Odesa Bay that has taken place in recent years did not stop, but only slowed down the process of the KE drying. As a result, ~800,000 tons of salt entering the estuary with seawater did not possible to reach a level of water salinity favorable for the development of biota – the main producer of the organic matters of medicinal peloids [20, 22].

In the summer seasons of 2015–2016 water salinity in the estuary water area varied within 230–381‰, in autumn – within 283–320‰, reaching 417–448‰ in the shallow waters of the northern part.

The average air temperature for the spring season of the specified period fluctuated in the range of 10,2-11,7°C. The warmest was the spring season of 2012, the average monthly temperature in May reached 19,4°C. In summer the highest average monthly air temperatures were characteristic for August 2010 (26,2°C) and July 2012 (25,7°C). The average air temperature in the autumn period of 2010 was 13,2°C, in 2012 – 14,3°C. The warmest autumn month during the research period was September 2012.

The average annual air temperature during this period varied in the range of 11,7-12°C and exceeded the climatic norm (10,6°C).

The average annual precipitation amounts in 2008-2009 were lower than the climatic norm, in 2010 and 2012 they exceeded the climatic norm and amounted to 742 mm and 526 mm respectively. Recent years were dry.

Under these conditions the species diversity of the algae species observed in different years differed greatly. The most diverse algal flora of KE was represented in the period of high water content in the estuary (2004–2006) along the water salinity gradient of 49,9–153,9‰ – 90 species (69 diatoms, 16 blue-green and 4 green algae). In 2005–2006 the number of algae species ranged from 55 to 58 during the period of low water level in 2008–2018 from 2 to 12 [20].

Our calculations indicate the existence of a relationship between water salinity and the number of algae taxa that appear under these conditions. The relationship between these indicators was inverse, and at the level of average strength ($r = -0,57$, $R^2 = 0,95$). *Rhoicosphenia abbreviata*, *Tabularia tabulata*, *Cylindrotheca closterium*, *Surirella striatula* Turpin, *Spirulina meneghiniana*, *Achnanthes brevipes*, *Stauropora salina*, *Dunaliella salina* were noted among the species with the highest physiological adaptability and rapid response to changes in the physical and chemical conditions of the environment. The last of the mentioned species turned out to be the most labile. It occurred in the water ecotopes of the KE basin in the salinity range of 5–345‰. During the period of seawater supply the number of species increased slightly due to the genera *Chaetoceros* and *Coscinodiscus*, etc. [20].

The results of photosynthetic pigments studies in the KE water and its main inflows are presented in Table 1, hydrochemical analysis of reservoir waters at monitoring stations – in Table 2. Investigating the concentrations of chlorophylls ("a", "b", "c") in the KE water area during 2008-2012 pp. we received the significant array of data that testify to a wide range of their indicators: chlorophyll "a" – from 0,09 µg/dm³ to 11,83 µg/dm³, chlorophyll "b" – from 0,21 µg/dm³ to 8,66 µg/dm³, chlorophyll "c" – from 0,86 µg/dm³ to 15,95 µg/dm³ (Table 1).

In the water inflows of KE the content of chlorophylls "a", "b" and "c" varied within the following limits: the Velykyi Kuyalnyk river — 0,26-12,5 µg/dm³, 0,10-0,55 µg/dm³ and 1,11 - 2,03 µg/dm³ respectively; Peresypski ponds — 0,29-2,30 µg/dm³, 0,59-2,38 µg/dm³ and 2,45-8,44 µg/dm³ respectively; Korsuntsivsky ponds — 0,48-2,63 µg/dm³, 1,40-5,02 µg/dm³ and 7,0-15,20 µg/dm³ respectively.

By our opinion the significant variability of microalgae communities' photosynthetic pigments concentrations of the shallow KE is related to dynamic changes in its abiotic conditions under the influence of climatic and anthropogenic factors.

Table 1

The pigment content in the KE and its water inflows in the period 2008-2012

Sampling date	Water body (for KE № of the observation station)	Pigments concentration, $\mu\text{g}/\text{dm}^3$			
		Chlorophyll «a»	Chlorophyll «b»	Chlorophyll «c»	Pheophytin
13.05.2008	Velykyi Kuyalnyk river	0,60	0,55	2,03	-
	KE, st. 12	1,21	1,46	5,95	-
	KE, st. 14	1,20	1,46	5,95	-
	KE, st. 5	1,30	2,37	8,90	-
	KE, st. 3	0,34	-	-	-
	KE, st. 4	0,34	-	-	-
	KE, st. 6к	0,34	-	-	-
	KE, st. 9к	10,44	-	-	-
	Korsuntsivsky ponds, st. 6	0,48	1,40	7,0	-
Peresyp ponds, st. 9	2,30	1,12	3,30	-	
15.08.2008	KE, st. 5	3,43	3,38	8,94	-
	KE, st. 12	0,50	0,79	1,90	-
	KE, st. 14	0,49	0,79	1,90	-
02.09.2008	Korsuntsivsky ponds, st. 6	1,66	5,02	7,96	-
24.10.2008	KE, st. 5	2,75	1,80	4,96	-
	KE, st. 12	3,11	2,79	8,16	-
	KE, st. 14	2,84	2,79	8,16	-
22.02.2009	KE, st. 5	3,82	2,05	14,6	2,35
24.02.2009	KE, st. 8	10,62	5,22	7,1	15,9
05.04.2009	KE, st. 5	2,23	0,71	-	3,38
	KE, st. 4	3,69	4,54	15,95	14,15
	Korsuntsivsky ponds, st. 6	2,63	4,60	15,20	-
	Peresyp ponds, st. 9	1,48	2,38	8,44	3,64
23.04.2009	KE, st. 12	0,18	-	-	1,16
	Peresyp ponds, st. 9	0,29	-	-	1,01
23.05.2009	KE, st. 14	1,20	-	-	-
03.06.2009	Velykyi Kuyalnyk river	1,31	0,1	1,13	1,85
02.07.2009	KE, st. 5	1,55	3,03	-	-
14.07.2009	KE, st. 3	1,96	8,66	-	-
	KE, st. 14	0,49	-	-	-
29.09.2010	KE, st. 13	0,09	0,21	1,27	-
	Peresyp ponds, st. 9	0,46	0,59	2,45	-
14.10.2010	KE, st. 12	0,21	0,22	-	-
	KE, st. 8	0,33	0,55	0,86	0,05
26.11.2010	KE, st. 9к	0,55	0,49	1,38	0,58
05.11.2010	KE, st. 5	1,0	0,44	1,0	1,75
12.11.2010	Velykyi Kuyalnyk river	0,26	0,39	1,11	0,17
25.04.2012	KE, st. 5	4,4	-	-	-
	KE, st. 12	11,83	-	-	-
	KE, st. 14	8,42	-	-	-
14.06.2012	KE, st. 14	1,62	-	-	-
12.10.2012	KE, st. 12	1,72	-	-	-
16.10.2012	KE, st. 9к	0,92	-	-	-
18.10.2012	KE, st. 5	1,39	-	-	-
	KE, st. 8	1,16	-	-	-

Table 2

The main physical and chemical parameters of the KE and its water inflows
in the period 2008-2012

Sampling date	Water body (for KE № of the observation station)	Dissolved oxygen, mg O ₂ /dm ³	Biochemical oxygen demand (BOD ₅), mg O ₂ /dm ³	Chemical oxygen demand (COD), mg O ₂ /dm ³	Temperature, °C	Salinity S, ‰	pH	NH ₄ ⁺ , mg N /dm ³	PO ₄ ³⁻ , mg P /dm ³
1	2	3	4	5	6	7	8	9	10
13.05.2008	Velykyi Kuyalnyk river	5,39	23,6	46,7	17	2,1	7,97	43,1	0,063
	KE, st. 12	3,13	32,9	488	23	207	7,50	24,3	0,135
	KE, st. 14	4,52	37,3	402	26	253	7,48	29,4	0,073
	KE, st. 5	5,80	29,2	231	22	206	7,83	33,2	0,079
13.05.2008	KE, st. 3	5,56	46,3	548	22	212	7,42	18,17	0,17
	KE, st. 4	5,39	42,3	443	23	208	7,45	34,12	0,15
	KE, st. 6к	4,87	32,9	242	23	200	7,71	38,52	1,31
	KE, st. 9к	5,39	23,6	176	23	201	7,56	55,36	0,19
	Korsuntsivsky ponds, st. 6	16,35	20,9	45,3	22	1,1	7,09	0,13	0,079
	Peresyp ponds, st. 9	17,74	7,7	15,1	16	2,3	7,80	0,13	0,294
	15.08.2008	KE, st. 5	5,57	34,9	432	32	266	7,04	61,1
KE, st. 12	4,0	43,4	368	33	298	7,18	15,7	0,079	
KE, st. 14	2,09	42,5	727	35	341	6,97	-	0,155	
02.09.2008	Korsuntsivsky ponds, st. 6	4,87	32,9	-	24	1,1	7,99	29,96	0,432
24.10.2008	KE, st. 5	5,57	34,9	452	14	194	7,70	61,14	0,049
	KE, st. 12	4,00	21,2	599	15	254	7,93	15,66	0,053
24.10.2008	KE, st. 14	3,65	31,8	361	17	267	7,42	8,32	0,155
22.02.2009	KE, st. 5	6,80	2,90	-	2	196	7,54	2,90	0,033
24.02.2009	KE, st. 8	9,40	5,00	-	2	115	7,54	1,17	0,039
05.04.2009	KE, st. 5	7,35	27,8	272	15,3	206	7,41	13,51	0,026
05.04.2009	KE, st. 4	-	-	-	15	-	-	-	-
	Korsuntsivsky ponds, st. 6	16,3	5,04	10,3	13	0,96	8,23	5,09	0,013
	Peresyp ponds, st. 9	14,80	3,1	6,3	13	2,2	7,61	0,039	0,139
23.04.2009	KE, st. 12	9,96	24,5	333	14	215	7,42	9,102	0,043
	Peresyp ponds, st. 9	-	-	-	7,5	1,8	-	-	-
23.05.2009	KE, st. 14	4,52	37,3	402	20	253	7,29	29,36	0,073
03.06.2009	Velykyi Kuyalnyk river	15,3	22,4	47	21	2,6	7,73	1,08	0,056
02.07.2009	KE, st. 5	-	-	699	25	235	7,42	9,58	0,129
14.07.2009	KE, st. 3	-	-	538	22	265	7,19	21,46	0,132
	KE, st. 14	3,65	-	555	35	299	6,96	12,36	0,459
29.09.2010	KE, st. 13	4,50	26,3	372	25	299	7,57	26,55	0,152
	Peresyp ponds, st. 9	17,70	6,4	11	17	1,1	7,93	0,436	1,874
14.10.2010	KE, st. 12	3,70	21,7	181	12,5	281	7,67	12,82	0,079
	KE, st. 8	4,80	24,1	350	15	266	7,63	11,63	0,224
05.11.2010	KE, st. 5	2,50	22,8	290	-	280	7,58	41,65	0,492
12.11.2010	Velykyi Kuyalnyk river	3,80	10,2	12,8	-	1,3	7,83	0,179	2,188

1	2	3	4	5	6	7	8	9	10
26.11.2010	KE, st. 9к	4,20	22,7	502	12	266	7,67	15,43	0,673
25.04.2012	KE, st. 5	-	-	-	25	-	7,34	-	-
	KE, st. 12	3,96	-	-	25	302	7,30	-	-
	KE, st. 14	4,77	-	-	29	341	7,30	-	-
14.06.2012	KE, st. 14	-	-	-	40	373	6,70	73,19	-
12.10.2012	KE, st. 12	-	-	-	19	259	7,65	45,08	-
16.10.2012	KE, st. 9к	-	-	-	23	351	7,63	42,14	-
18.10.2012	KE, st. 5	-	-	-	15	141	8,16	14,29	-
	KE, st. 8	-	-	-	19	368	7,56	18,69	-

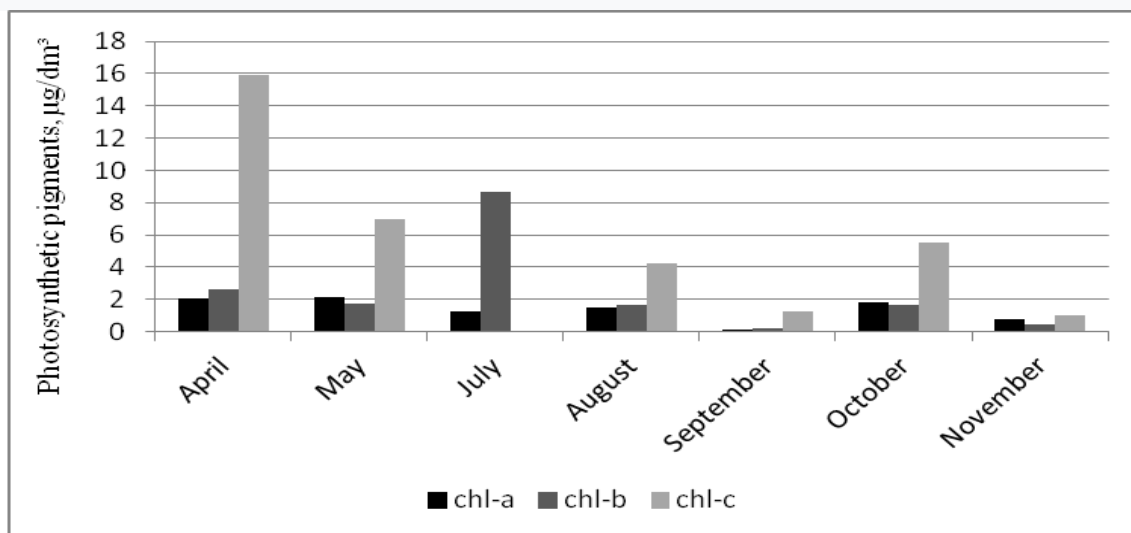


Fig. 2 – Intra-annual changes of chlorophylls "a", "b", "c" concentrations in the Kuyalnyk Estuary (according to averaged data in the period 2008-2010).

The dynamics of synchronous seasonal changes in the chlorophylls "a", "b", "c" content in KE in the period 2008-2010 is presented in Fig. 2. In general, increased concentrations of chlorophyll were observed in the spring, early summer, and mid-autumn (Fig. 2) and corresponded to the seasonal trend in the number and biomass of algae [22].

It should be noted that the presence of chlorophyll "b" indicates the development of the flagellated green algae in the research area, but the chlorophyll "c" – the diatom algae [23]. Thus, the composition of photosynthetic pig-

ments is largely determined by the systematic affiliation of algae (Table 3).

It should be noted that the part of chlorophyll "c" dominates during all seasons of 2008-2010, which indicates a decrease in photosynthetic activity during the period of the estuary salinization, as also indicated by the degradation of algocenosis [20, 22]. In this case the adaptive mechanisms of algocenosis are expressed in the growth of the auxiliary photosynthetic pigments "b" and "c" role.

In the KE water area the maximum concentrations of chlorophyll "b" ($8,66 \mu\text{g}/\text{dm}^3$)

Table 3

The content of photosynthetic pigments with different ratios of microalgae groups in the KE in May 2008 (based on averaged data)

Bacillariophyta	Cyanophyta	Chlorophyta	Chlorophyll «a»	Chlorophyll «b»	Chlorophyll «c»	Σ chlorophyll
%			$\mu\text{g}/\text{dm}^3$			
75	17	8	2,2	1,8	6,9	10,9

were observed in July 2009, the minimum (0,21-0,22 $\mu\text{g}/\text{dm}^3$) in September-October 2010. The maximum concentrations of chlorophyll "c" (14,60-15,95 $\mu\text{g}/\text{dm}^3$) were recorded in the winter-spring period of 2009, the minimum (0,86-1,0 $\mu\text{g}/\text{dm}^3$) – in October-November 2010.

During this period an increased amount of additional pigments (chlorophylls "b" and "c") was revealed in the waters of high salinity. The percentage of chlorophyll "b" were 10-31,6% of the total amount, chlorophyll "c" – 30,9-71,3%. At the same time, in almost all years and seasons the importance of chlorophyll "c" in the pigment deposits observed.

It was the evidence that the main mass of the algocenosis of the KE was mainly composed by diatom algae due to the periods of extremely high salinity of water (close to 300‰ and higher when in the water area of the estuary dominated mainly the green flagella and the *Dunaliella Salina Teod.* that had been confirmed by the results of the algal flora is monitoring maintained in the same time [20, 22, 23].

The ratio of chlorophyll "c" to "a" in the KE varied during that period from 0,67 to 6,85. The increase in the ratio is probably associated with a faster decomposition of chlorophyll "a" compared to chlorophyll "c" [16-19], which allows us to judge about the physiological state of phytoplankton. The ratio of the chlorophyll "a" to chlorophyll "b" concentration, which characterizes the potential photosynthetic activity of microalgae (the higher the ratio – the higher the activity), fluctuated in the KE water area in the range of 0,23-3,14 and in almost 53% of cases did not exceed 1, that indicates the low potential photosynthetic activity of algocenosis in conditions of low water content in the estuary and high water salinity.

Another important indicator of the microalgae communities physiological state is the pheophytin content [16, 18]. As we mentioned above, when the ratio of the chlorophyll "a" content to pheophytin is < 1 , algae decomposition processes dominate in the water body. The proportion of pheophytin less than 40% of the total pigments amount corresponds to the active state of phytoplankton, an increase in the proportion of pheophytin to 40-65% already indicates a suppressed state of communities with reduced physiological activity and low production potential, and with a proportion of $> 65\%$, algae cells no longer have the necessary photosynthesis potential [14, 16, 17, 18].

According to the data of experimental studies in the winter-spring period of 2009 and

autumn of 2010 the part of pheophytin in the water area of KE during this period fluctuated in the range of 2,87-69,30%. At the same time, in October-November 2010 the share of pheophytin varied from 2,87 to 23,78% that corresponds to high production potential and the winter-spring period of 2009 was characterized mainly by a decrease in production potential. During this period the processes of destruction of microalgae communities dominated, that was also confirmed by algofloristic research data [20, 22, 23].

In 2015 and 2016 according to the authors [19] after filling the estuary in winter and spring periods with sea water from the Odesa Bay the concentration of chlorophyll "a" increased slightly and ranged from 1,1 to 57,6 $\mu\text{g}/\text{dm}^3$, and the pheophytin - from 1,0 to 38,4 $\mu\text{g}/\text{dm}^3$. The maxima of chlorophyll "a" were observed in April ($> 25 \mu\text{g}/\text{dm}^3$) and were characteristic for hypertrophic water bodies. The analysis of the ratio of the pheophytin to chlorophyll "a" concentration shown that in 2015 from July to December and in 2016 from July to November the greatest degradation of microalgae communities was noted.

It should also be noted that in the spring of 2015-2016 we observed the blooming of *Dunaliella salina* in the southern part of the estuary water area, that is also indicated by the increased content of chlorophyll "a".

The correlation analysis of photosynthetic pigment relationships showed that the closest positive relationship was observed between the concentrations of chlorophyll "a" and chlorophyll "b" ($r = 0,535$). The correlation between the concentrations of chlorophylls "a" and "c" was 0,467, and between chlorophylls "b" and "c" – 0,698. The correlation coefficient between the concentrations of pheophytin and chlorophylls "a" and "b" was 0,837 and 0,967 respectively.

The time changes of chlorophyll "a" concentration in many respects repeats changes in water temperature and salinity. In April-May along with the warming and lowering of water salinity (and as the result increase in the photosynthesis intensity) the concentration of chlorophyll "a" also increases (Table 1).

Suppression of the algal flora development in the KE is already observed at a salinity of 200‰ [20] (Fig. 3).

For the KE the seasonal spatial differences in the chlorophyll "a" concentration are quite typical across the water area (Fig. 4 A, B, C).

Spatial distribution is characterized by spotting, especially in spring (Fig. 4 A). Increased concentrations of chlorophyll "a" were observed in the spring in the southern, central

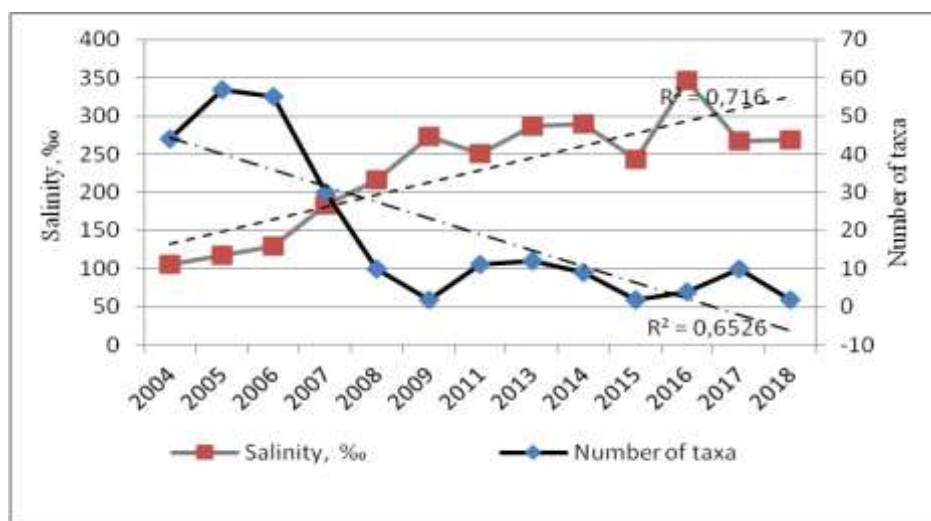


Fig. 3 – Synchronous changes of algae species diversity and water salinity in the KE in 2004–2018 (according to averaged data during the algal flora research period [20])

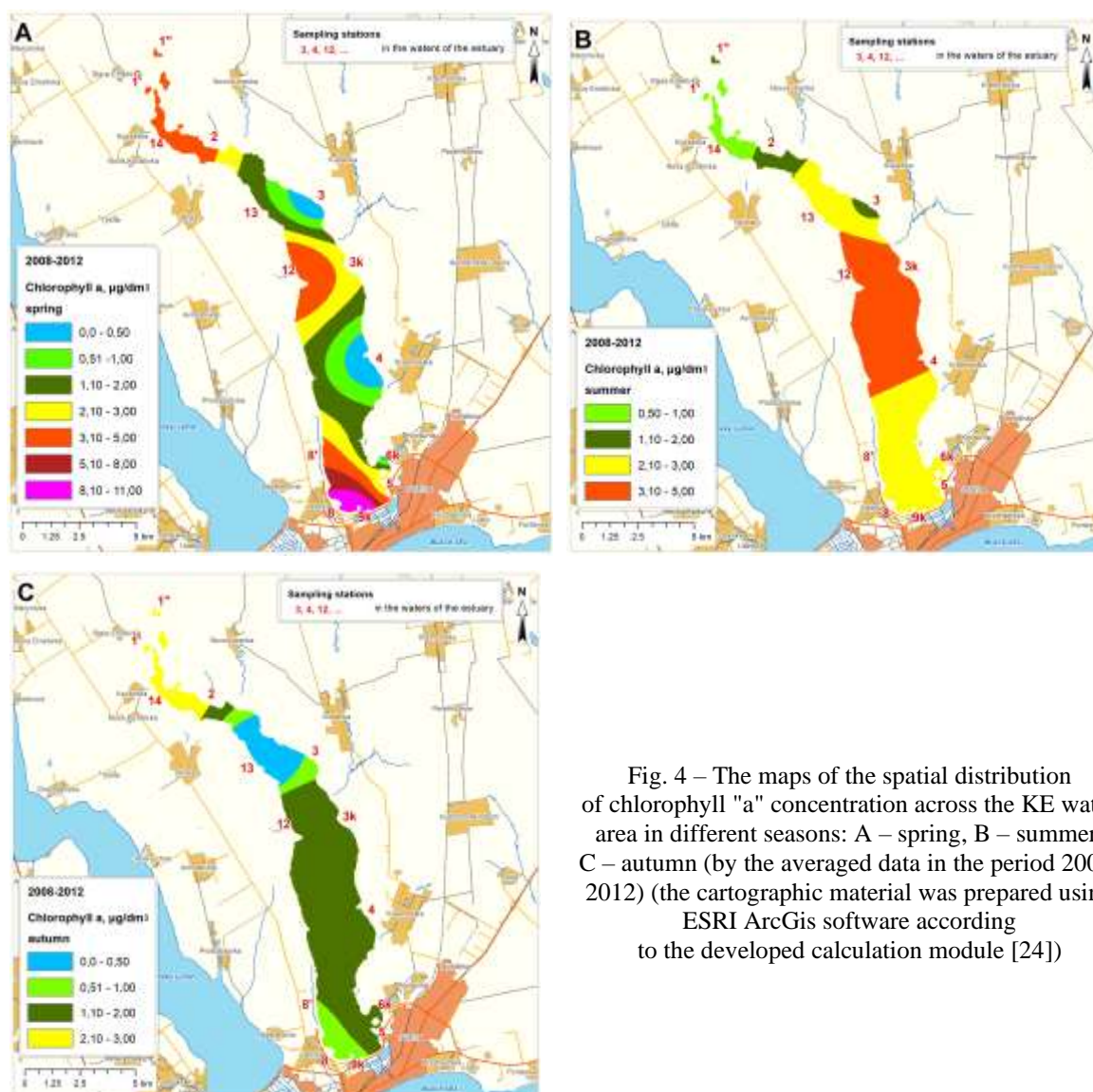


Fig. 4 – The maps of the spatial distribution of chlorophyll "a" concentration across the KE water area in different seasons: A – spring, B – summer, C – autumn (by the averaged data in the period 2008-2012) (the cartographic material was prepared using ESRI ArcGis software according to the developed calculation module [24])

parts of the estuary water area and in the upper part of the estuary, mainly near mouths of river (station 14, 3k), near ponds (stations 9k, 6k) and streams (station 12) enters. In summer the distribution of chlorophyll "a" was more uniform with a maximum in the central part, in autumn an increased content of chlorophyll "a" was observed in the shallow water in the top part of the estuary.

In general, the high content of pheophytin in the KE water area (Table 1) indicates that during the period of the conducted research (2008-2012) there were unfavorable conditions for algal bloom, which is completely consistent with the data of previous research in the first two decades of the 21st century. [20, 22, 23].

The data we obtained show that the content of chlorophyll "a" in the water area of the KE and its main inflows is determined by a complex of abiotic factors: first of all - lighting conditions, temperature, oxygen and salt regimes, and the content of biogenic substances.

Thus, according to the results of research in May 2008 the close direct correlation was registered between the content of chlorophyll "a" in plankton and suspended particles in water of the KE ($r = 0,938$), ammonium nitrogen ($r = 0,811$), silicon soluble in water ($r = 0,808$), dissolved oxygen ($r = 0,588$) and inversely with BOD₅ ($r = -0,715$) and COD ($r = -0,582$). The similar correlations were registered in all seasons of 2008, but of different strength.

In general, the level of the chlorophyll "a" content corresponds to the dynamics of changes in salinity and water temperature (Fig. 5). On the monthly averaging scale the correlation coefficients of the chlorophyll "a" concentration and the salinity and temperature of water of the KE are $-0,37$ and $-0,55$ respectively (at 95% level of significance). When the time scale of averaging increases, the closeness of the correlations increases too.

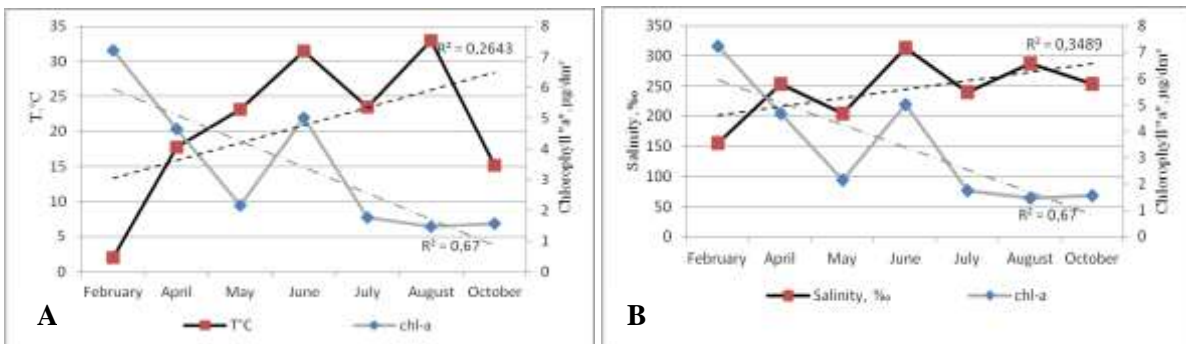


Fig. 5. The dynamics of average monthly changes: A – chlorophyll "a" and water temperature; B – chlorophyll "a" and water salinity of the KE in the period 2008-2012

With seasonal averaging the correlation coefficients were $-0,63$ and $-0,82$ respectively (at the same level of significance). Relatively low values of the chlorophyll "a" content in KE water during the study period were due to high water mineralization, which negatively

affects the development of algal flora [20]. A significant excess of the chlorophyll content in the sum with pheopigments in comparison with the content of chlorophyll "a" in the phytoplankton of the KE indicates unfavorable conditions of existence for algal flora.

Conclusions

As a result of conducted research new data were obtained about the content of photosynthetic pigments (chlorophyll "a", "b", "c") in the KE during the period of low water level (2008-2012) and its main water inflows, and about features of the chlorophyll "a" spatial distribution in different seasons of the year.

The ratio of photosynthetic pigments and their decomposition products in the period

of low water content and high salinity of the KE waters indicate that in such conditions, in most cases, the processes of destruction of microalgae groups dominate over the production processes. The correlation between pigment concentrations is characterized by high correlation coefficients at the level of 0.467-0.698 in the long-term aspect.

A high correlation is revealed between the main photosynthetic pigment (chlorophyll "a") and its decomposing product pheophytin ($r = 0,837$).

Adaptive mechanisms of microalgae groups in relation to high salinity conditions are expressed in an increase in the proportion of auxiliary pigments relative to chlorophyll "a".

According to the results of correlations between the content of chlorophyll "a" and abiotic factors of the environment for the growth of microalgae communities have been

revealed a number of main indicators (temperature, salinity, oxygen regime and regime of biogenic substances) that significantly affect photosynthetic activity, KE productivity, structure and species composition of algalocenosis.

The results of the KE pigment fund study indicate that the characteristics of the content of photosynthetic pigments and their ratio can be used to identify periods and zones of disturbance of ecological conditions in the reservoir and are sufficiently informative characteristics of the functioning of the reservoir.

Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancies have been completely observed by the authors.

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ДОСЛІДЖЕННЯ ФОТОСИНТЕТИЧНИХ ПІГМЕНТІВ В ГІПЕРГАЛІННОМУ КУЯЛЬНИЦЬКОМУ ЛИМАНІ ТА ЙОГО ПРИПЛИВАХ (УКРАЇНА, ПІВНІЧНО-ЗАХІДНЕ ПРИЧОРНОМОР'Я)

Мета. Дослідити вміст фотосинтетичних пігментів (хлорофілу «а», «b», «с» і феофітину) у гіпергалінному Куяльницькому лимані (Кл) та основних його припливах в період низької водності лиману (2008-2012 рр.), оцінити динаміку міжрічних та внутрішньорічних концентрацій, їх просторовий розподіл по акваторії Кл та виявити вплив абіотичних чинників водного середовища на зазначені характеристики.

Методи. Гідрохімічні, гідробіологічні методи аналізу, геоінформаційний просторовий аналіз та статистичний аналіз. Використано оригінальну геоінформаційну базу даних комплексного багаторічного (2000-2022 рр.) моніторингу басейну Куяльницького лиману.

Результати. За результатами узагальнення, аналізу та систематизації матеріалів експериментальних досліджень вмісту фотосинтетичних пігментів (хлорофілу «а», «b», «с») і феофітину (первинного продукту розпаду хлорофілу) у поверхневих водах гіпергалінного Куяльницького лиману (Кл) і його основних припливах (р. Великий Куяльник, канали стоків з Пересипських та Корсунцівських ставків) у період низької водності лиману (2008-2012 рр.) представлено міжрічний та внутрішньорічний розподіл вмісту пігментів, оцінено їх співвідношення в зазначених водних об'єктах та просторовий розподіл вмісту хлорофілу «а» по акваторії Кл в різні сезони року. Встановлено, що в періоди низької водності Кл та осолонення його вод продукційна діяльність незначна, але вона не припиняється. Адаптивні механізми водоростевих угруповань щодо екстремальних умов Кл (осолонення, обміління, підвищення температури води, скорочення притоку прісних вод) виражаються в збільшенні долі допоміжних пігментів (хлорофілів «b» і «с»). Отримані співвідношення пігментів вказують в основному на домінування водоростей відділу діатомових у всіх водних об'єктах басейну протягом періоду досліджень. Проведено кореляційний аналіз взаємозв'язків між концентраціями хлорофілів а, b, с; концентраціями окремих хлорофілів і феофітину та між хлорофілом «а» і основними абіотичними чинниками середовища (температура, рН, розчинений у воді кисень, БСК₅, ХСК, азот амонійний, фосфор фосфатний, кремній розчинний). Результати досліджень свідчать про низьку фотосинтетичну діяльність водоростей Кл та переважання процесів деструкції в період низької водності та осолонення лиману.

Висновки. На підставі даних багаторічних спостережень досліджено зв'язки між вмістом хлорофілу «а» і абіотичними чинниками середовища зростання угруповань мікроводоростей та виділено ряд основних показників (температура, солоність, кисневий режим і режим біогенних речовин), які суттєво впливають на фотосинтетичну активність, продуктивність Кл, структуру та видовий склад альгоценозу. Результати дослідження пігментного фонду Кл свідчать про те, що характеристики вмісту фотосинтетичних пігментів та їх співвідношення можуть бути використані в якості інтегральних характеристик продуктивності та екологічного стану водойм.

КЛЮЧОВІ СЛОВА: хлорофіл «а», «b», «с», феофітин, співвідношення, Куяльницький лиман, припливи, абіотичні чинники, міжрічна динаміка, внутрішньорічна динаміка, просторовий розподіл

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