ЕКОЛОГІЯ ОКЕАНІВ ТА МОРІВ

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RESULTS OF PHYTOPLANKTON PIGMENTS STUDIES IN THE ZMIINYI ISLAND COASTAL WATERS IN THE BLACK SEA, 2004-2012

The data on photosynthetic phytoplankton pigments in coastal waters of the Zmiinyi Island in 2004-2012 were analysed in details. Results of studies of Chl *a*, Chl *b*, Chl *c*, pheophytin *a* concentrations and Margalef's pigment diversity index inter-seasonal and inter-annual changes and trends have been presented. The fact of positive trend in Chl *c* discovered for the first time can indicate the structural changes taking place in the Black Sea phytoplankton community during past years.

Keywords: Black Sea, pigments, chlorophyll, phytoplankton, Zmiinyi Island

INTRODUCTION

As is known [11, 23, 29], photosynthetic phytoplankton pigments (PSPs), such as chlorophylls *a, b, c*, are specific markers characterizing the processes taking place in marine phytoplankton and enabling us to assess its structure and biomass [2, 22, 25]. As the studies of phytoplankton community state using assessment of its PSPs are more objective and less time-consuming compared with classic microscopy methods, PSP is the most efficient in marine areas where eutrophication happens. In particular, one of such areas is the Black Sea [4], where eutrophication not only brings down marine environment quality causing blooms of phytoplankton, but also gives rise to hypoxia and mass mortalities of marine organisms. In the recent years potentially dangerous and toxic microalgae are emerging of in the Black Sea coastal areas more often [19, 24]; their control is efficiently carried out using chemotaxonomic markers, which are the PSPs [13].

Observations of photosynthetic pigments content in the Black Sea waters began in the 60th [7] and were performed in different parts of the Black Sea till the end of the 90th [28, 30, 3]. After demise of the USSR those observations in marine economic zones of Ukraine, Russia and Georgia practically stopped. However, they went on in marine economic zones of Bulgaria, Romania and Turkey, where PSPs, in particular Chl *a* content in marine water became widely used to determine the unwanted disruptions in the Black Sea marine ecosystem [1, 21, 27,10, 26, 4, 6, 14, 20].

Of special interest are the regular studies of phytoplankton community state and PSPs in the deltaic and open parts of the sea, also influenced by river flow. Unique location of the "Zmiinyi Island" Marine Research Station (MRS) of Odessa National

I. I. Mechnikov University (ONU), where regular observations of phytoplankton community state and the PSPs have been performed from 2004 till 2012 in the framework of the Programme for Integrated Monitoring of the Zmiinyi Island Coastal Waters [32, 15, 16] enables us to control the state of open marine waters ecosystem influenced periodically by brackish river waters. Sets of regular experimental data about oxygen, total nitrogen, total phosphorus and Chl *a* content have been used to assess water quality with the triple exponential moving average (TRIX) index [16].

The aim of our work has been to study the PSPs inter-annual and seasonal changes and trends, such as Chl *a,* Chl *b,* Chl *c* and Pheophytin *a* in the Zmiinyi Island coastal waters in 2004-2012.

MATERIALS AND METHODS

Study Area.

Observations have been regularly performed at Marine Research Station (MRS) "Zmiinyi Island" of the ONU. The Zmiinyi Island (45°15'22.0" N and 30°12'03.8" E) is situated in the north-western part of the Black Sea (NWBS) about 35-40 km far from the Danube Delta.

SAMPLING AND ANALYSIS

Integrated monitoring programme of the MRS "Zmiinyi Island" included sampling and determination of hydrological, hydrochemical parameters (temperature, salinity, oxygen, pH, nutrients concentrations) and PSPs (Chlorophyll *a, b, c* and Pheophytin *a*). Sampling was performed at surface (0.5 m) and bottom (about 8 m) layers using Hydro-Bios bathometer. Oxygen content, salinity, pH, temperature, total nitrogen (TN), total phosphorus (TP) and other hydrological and hydrochemical parameters were measured every decade using [8]. The PSPs were determined using [31] and [9].

Marine water, 2-4 l in volume, was filtered immediately after sampling through nitrocellulose filters manufactured by Sartorius Company (pore diameter 0.8 μm) and stored in exsiccator in a fridge for not longer than one month before analyses. Pigments were extracted in 90 % water solution of acetone, than the extraction was clarified by centrifugation at 6000 rpm during 10 minutes. Optical density of extraction was measured using photometer JENWAY-6300. Concentrations of chlorophylls *a, b* and *c* were calculated using SCORE-UNESCO equations [31]. Pheophytin *a* quantitative content was calculated using equation [17]. Margalef's pigment diversity index – MPBI [18] was determined by the ratio of values at 430 and 665 nm.

MATERIALS

The results of regular PSPs observations in the Zmiinyi Island coastal waters, the temporal distributions of which in the period 2004-2012 are presented on Figures 1-3, have been the source data for this study. Determination of photosynthetic pigments (chlorophylls *a, в, c, a*, as well as Pheophytin *a*) was performed regularly every 5 days in the period from 2004 till 2008 and every 10 days from 2009 till 2012 (654 samples) in surface (0.5 m) and bottom (8 m) horizons. The same samples were used to determine the main hydrophysical and hydrochemical parameters, such as salinity, temperature, pH, transparency, oxygen and nutrients content.

STATISTICAL ANALYSIS

Standard statistical approaches including correlation analysis ($p < 0.05$) have been applied to find interrelationships between studied constitutes. Significance tests for comparison of the average values using Student t-test (normal distribution) have been calculated. All the analyses have been carried out with STATISTICA (version 6.1 for Windows, StatSoft, Inc., 1984 – 2004). Graphical visualisation has been carried out using MS Excel 2003.

RESULTS AND DISCUSSION

As is known [11, 12], Chl *a* is contained in practically all the algal species, while presence of Chl *b* or Chl *c* enables us to divide phytoplankton community into pigment groups. That is why we have paid special attention to analyses of Chl *a, b, c*, Pheophytin *a* and pigment index temporal distributions in different seasons and to the changes in their ratios depending on seasons and on changing physicochemical conditions.

Table 1 and Figures 1-3 present the results of experimental determinations of Chl *a, b, c*, Pheophytin *a* and the values of pigment index in 2004-2012, the analyses of which have shown that maximal changeability of all the studied PSPs' concentrations are observed in the surface layer. At that, Chl *a* concentrations in surface layer varied between 0.07 (30.05.11) and 28.03 (5.06.2005) with average value 1.60±2.76; Chl *b* – from 0.05 (20.09.11) to 14.09 (20.07.2005) with average value 0.79±1.24; Chl *c* – from 0.01 (05.11.2005, 15.05.2006) to 6.11 (20.11.2010) with average value 0.60±0.63; Ph *a* – from 0.04 (25.07.2006) to 18.24 (30.05.2009) with average value 1.25±2.26 and pigment index – from 2.0 (5.04.2006) to 6.7 (25.08.2006) with average value 3.01 ±0.57.

Table 1.

Range of Changes, Average Values and Standard Deviations of PSPs Concentrations in the Surface / Bottom Marine Waters Near the Zmiinyi Island in 2004-2012

Parameter	Quantity of Observations	Minimal	Maximal	Average	STD
Chl *a*, μg L^{-1}	662	0.07/0.05	28.03/14.84	1.60/0.95	2.76/1.28
Chl *b*, μg L^{-1}	662	0.05/0.02	14.09/3.96	0.79/0.49	1.24/0.49
Chl c, μg L^{-1}	662	0.01/0.01	6.11/4.42	0.60/0.55	0.63/0.58
Pheophytin, μg L^{-1}	662	0.04/0.02	18.24/10.87	1.25/0.75	2.26/1.11
Pheophytin, %	662	6.60/2.90	92.20/94.50	41.90/42.52	19.17/20.0
MPDI	620	2.0/2.2	6.7/6.3	3.2/3.3	0.5/0.5

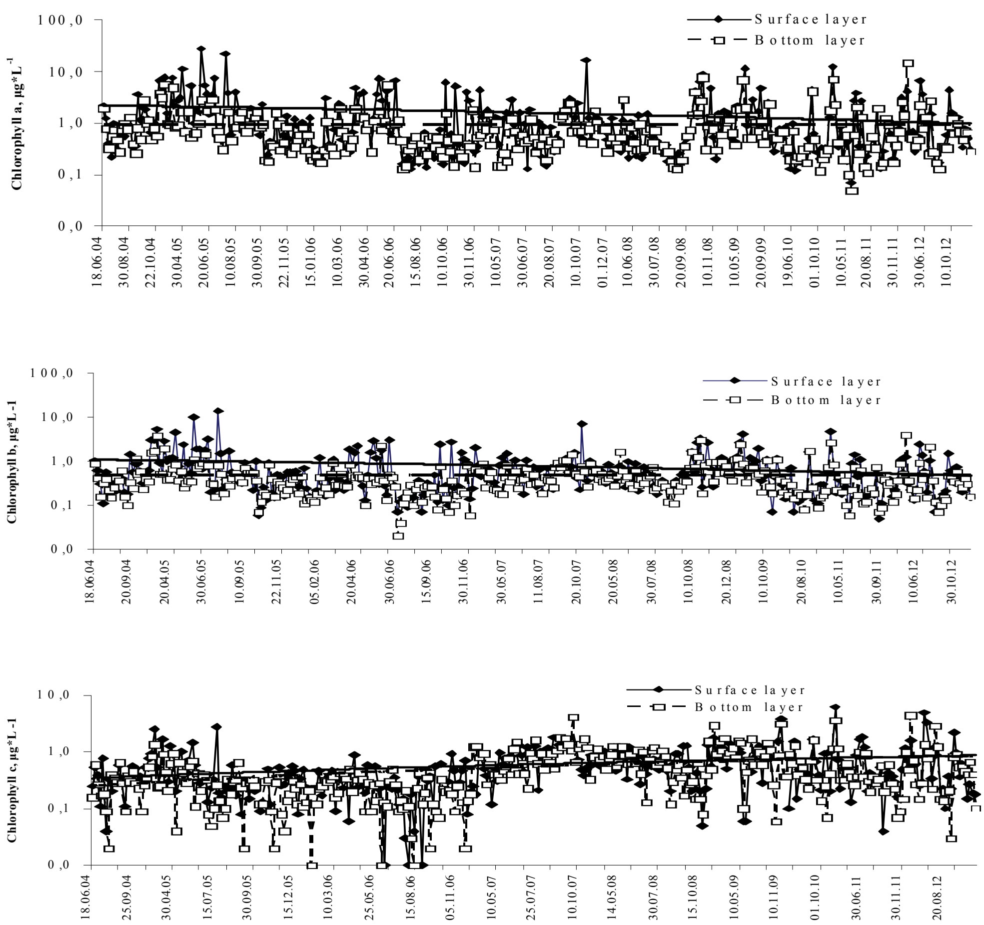
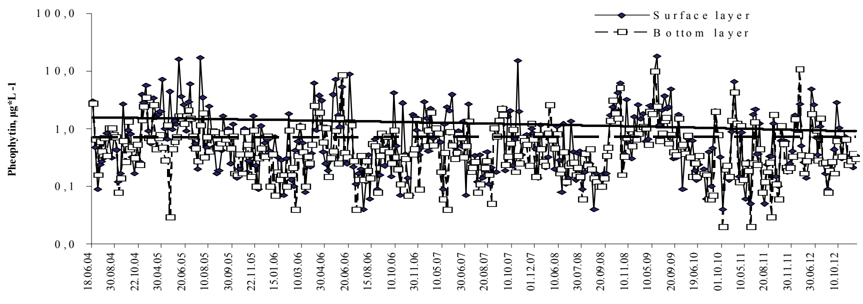


Fig. 1. Distribution of Chl a, Chl b and Chl c concentrations in the surface and bottom waters of the sea near the Zmiinyi Island coast in 2004-2012

Chl *a,* Chl *b,* Chl *c* concentrations in the surface layer were in the average higher than in the bottom layer 1.7, 1.6 and 1.2 times respectively. Average Pheophytin *a* concentration in the bottom layer, similarly to Chl *a*, was 1.7 times lower than on the surface, but Pheophytin relative content at the bottom was 0.6 % higher than at the surface. Pigment index, as well as Pheophytin relative content, in the bottom layer was insignificantly higher than in the surface one. Significant trends of decrease in Chl *a* and Chl *b* concentrations and increase in Chl *c* concentrations were observed in PSPs concentrations distribution for the entire period of observations, both in the bottom and surface layers. Long-term changes in Pheophytin and MPDI were not so significant.



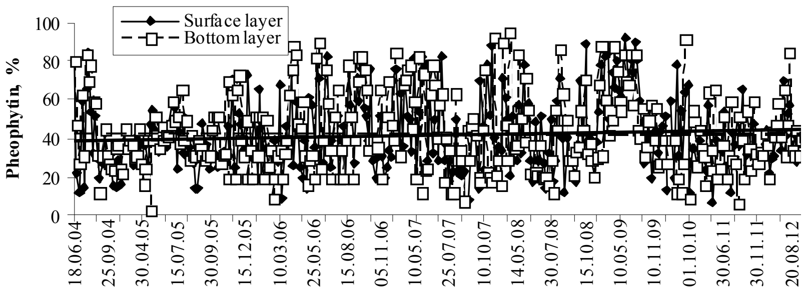


Fig. 2. Distribution of Pheophytin a absolute and relative concentrations in the surface and bottom waters of the sea near the Zmiinyi Island coast in 2004-2012

Taking into account high changeability of the studied parameters, as well as the fact that in 2004 – 2008 sampling was done every 5 days, while in 2009 – 2012 every 10 days, i. e. in different periods observations were performed with different intervals, we used average monthly values of each studied parameter to analyse seasonal and inter-annual changes and to assess trends.

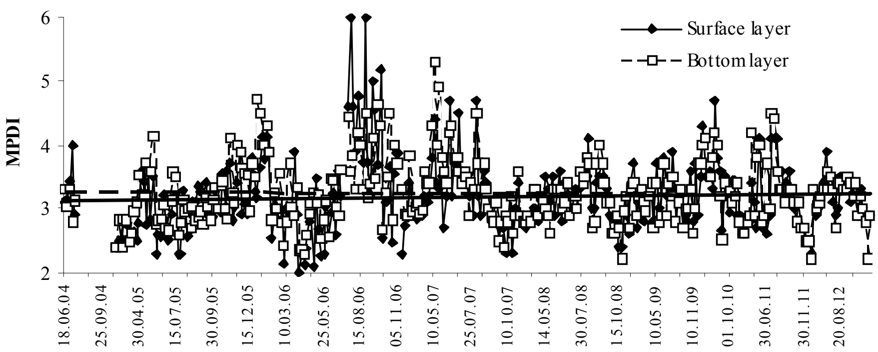


Fig. 3. Distribution of MPDI values in the surface and bottom waters of the sea near the Zmiinyi Island coast in 2004-2012.

Chlorophyll a

Analysis of Chl *a* average monthly concentrations distribution in the surface and bottom water layers near the Zmiinyi Island coast for 2004 – 2012 (see Fig. 4) has shown that changes of Chl *a* concentrations were happening synchronously enough in both layers (correlation coefficient $r=0.72$, $p<0.01$).

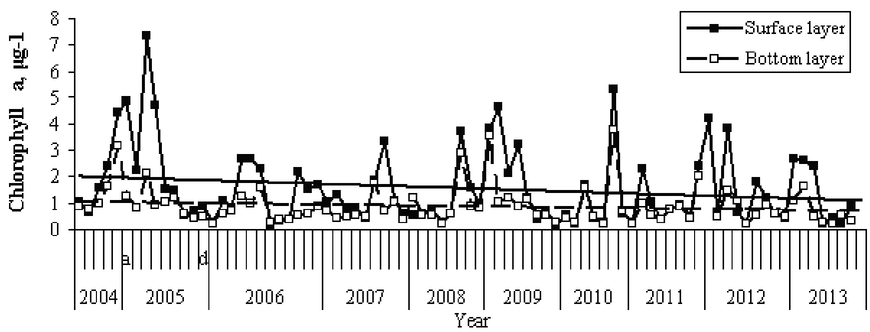


Fig. 4. Distribution of Chl a average monthly concentrations in the surface and bottom water layers near the Zmiinyi Island coast in 2004 – 2012.

Average monthly Chl *a* content varied within broad range, at that maximal values were registered in June 2005, 2009, 2012 (7.33±9.36; 4.60±5.89 and 3.82±2.75 µg/l respectively) and in November 2010 and 2004 (5.30±6.09 and 4.43±3.71 µg/l respectively), while minimal values were observed in July 2006 and 2010 (0.17±0.03 and 0.22±0.06 µg/l respectively), in August 2012, 2008, 2006 and 2011 (0.23±0.10; 0.26±0.08; 0.35±0.19 and 0.39±0.09 µg/l respectively) and January 2006 (0.26±0.07 µg/l).

Chlorophyll b

Average monthly Chl *b* concentration values in the surface and bottom waters are presented in Fig. 5. Content of this pigment in plankton was in average 2 times less than that of Chl *a*, but together with that their variations were synchronous, the evidences of which were high correlation coefficients both in the surface ($r=0.96$) and in bottom waters ($r=0.93$). Chlorophyll *b* content in the surface water layer was in average 1.6 times higher than in the bottom layer, which was also characteristic of Chl *a*. The range of Chl *b* average monthly values changes was 2 times lower than that of Chl *a*, however most of concentration peaks, like with Chl *a*, fall on June (2.88±3.30 µg/l in 2005; 1.82±2.0 µg/l in 2009; 1.47±0.93 µg/l in 2012) and November (2.02±2.32 µg/l in 2010; 2.42±2.20 µg/l in 2004); minimal concentrations were registered in winter period and in August. Thus, seasonal variations of Chl *b* (see Fig. 5) repeated the regularities inherent in Chl *a* with two maximums in spring-summer and autumn periods.

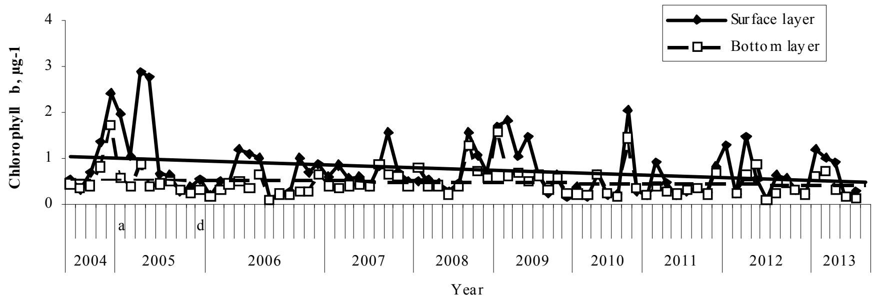


Fig. 5. Average monthly Chl b concentration values in the surface and bottom waters of the sea near the Zmiinyi Island coast in 2004-2012.

Chlorophyll c

Chl *c* average monthly concentrations in the surface and bottom layers for the studied period (2004-2012) are presented in Fig. 6. Minimal (1.2 times) excision of surface layer concentrations compared to bottom ones is characteristic of Chl *c*. Its content compared to Chl *a* was in average 2 times lower and equalled to Chl *b* content. Average monthly content of Chl *c* varied within the range of Chl *b* concentrations; maximums were registered in June and November, like with two other chlorophylls. Together with this, we should note peculiarity of the dynamics of Chl *c* maximal concentrations, which grew from 1.24±2.39 µg/l in November 2004 to 2.31±2.06 –2.63±3.02 µg/l in 2009-2010 and reached the highest values (3.07±1.87 µg/l) in June 2012.

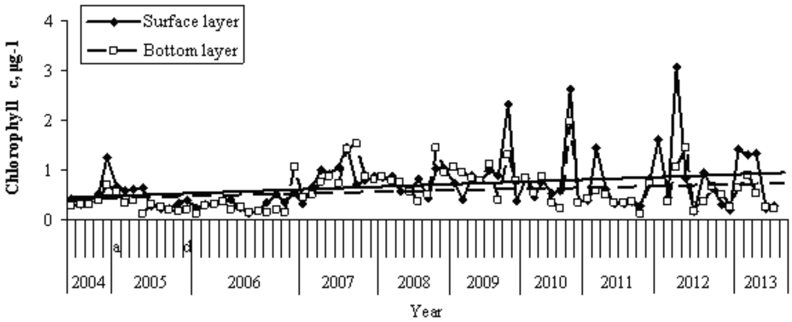


Fig. 6. Average monthly Chl c concentration values in the surface and bottom waters of the sea near the Zmiinyi Island coast in 2004-2012

Pheophytin a

Average monthly values of Pheophytin *a* concentrations and relative content in the surface and bottom water layers for the studied period are presented in Fig. 7. The biggest range of variations of this pigment was characteristic of the surface layer, where in June 2009 its highest concentration was registered (7.18±9.59 µg/l). High

Pheophytin *a* concentrations (4.79±2.72; 2.70±3.59 and 2.72±2.06 μg/l) were also registered in June 2005, 2006 and 2012 respectively. Bimodal curve with first maximum in spring-summer period and second in October-November is characteristic of Pheophytin *a* seasonal dynamics like that of chlorophylls. The autumn maximum of concentrations was characterized by lower peaks of concentration, which made 3.16±5.38 μg/l (October 2007) and 2.91±3.14 μg/l (November 2010). Pheophytin *a* concentrations dynamics of many years is marked by weak negative trend for the surface waters, while no trend was revealed for the bottom layer. Analysis of dynamics of Pheophytin *a* relative content average monthly values in marine plankton has shown that Pheophytin relative content varied within broad limits from 19.0-20.0 % (July 2008 and August 2010, 2011) to 81.8-84.3 % in June-July 2009. It is worthy of note that in the period 2004-2008 high values of Pheophytin *a* relative content (66.5-75.2 %) was characteristic of bottom waters, while in 2009-2012 maximal values were registered in the surface layer. Analysis of Pheophytin relative content dynamics of many years revealed no significant trends.

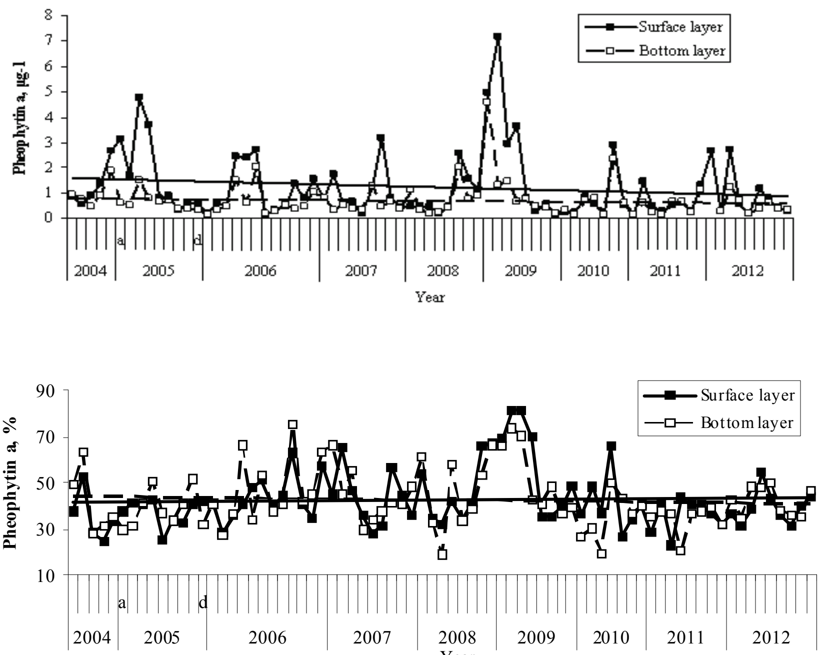


Fig. 7. Distribution of Pheophytin a average monthly concentrations and relative content in the surface and bottom water layers near the Zmiinyi Island coast in 2004-2012

Margalef's pigments diversity index (MPDI)

Average monthly MPDI values in the surface and bottom waters of the sea in 2004-2012 are presented in Fig. 8. Changes in values of the index in both layers were taking place synchronously enough, which was proved by high value of correlation coefficient (r=0.81, p<0.01). The highest MPDI average monthly value made 5.1 and was registered in July 2006. High values of the index within the range 4.0-4.3 were received also in January (2006), May (2007), June (2010) and August (2006). The lowest MPDI average monthly values from 2.3 to 2.4 were characteristic of spring months (March 2012, April 2006) and also October 2004. No pronounced trends in the MPDI dynamics of many years were revealed.

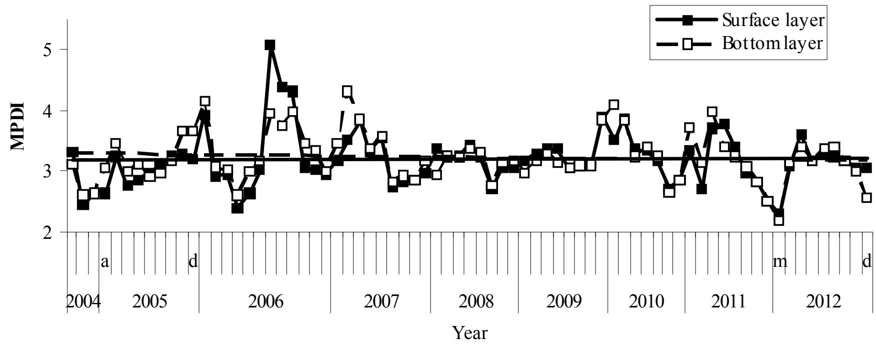
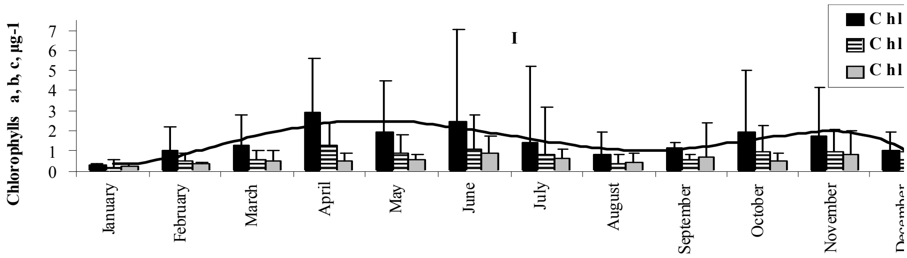


Fig. 8. Average monthly MPDI index distribution in surface and bottom waters of the sea near the Zmiinyi Island coast in 2004-2012.

Seasonal changes

To assess the statistically significant intra-annual seasonal changes we averaged the data for each parameter studied for each month of 2004-2012 (see Fig. 9-11). Analysis of seasonal variation of Chl *a* concentration in the surface water layer revealed bimodal distribution with maximums in spring-summer and autumn periods (see Fig. 9), which was earlier observed in the eastern and western parts of the Black Sea in the 1980th [3]. Maximal concentrations of Chl *a* in the surface water layer was registered in April (2.91±2.70 μg/l) and June (2.50±4.58 μg/l), while the second maximum observed in October and November was 1.5 times lower and made respectively 1.93±3.09 μg/l and 1.73±2.47 μg/l. Minimal concentrations of Chl *a* were registered in January and August: 0.26±0.07 and 0.80±1.10 μg/l respectively. In the bottom layer of water the range of seasonal variations was similar to that in the surface layer, but much smaller in values. Spring (April, 1.18±0.43) and autumn (November, 1.17±1.53 μg/l) maximums of Chl-*a* in the bottom layer were 2.5 times lower than in the surface layer during the same period. Minimal average monthly concentrations of Chl *a* in the bottom layer equalled in January to 0.21±0.05 μg/l and in July-August to 0.63±0.57 μg/l and were approaching concentrations in the surface layer.

In Chl *b* and Chl *c* seasonal variations of concentration, similarly to those of Chl *c*, bimodal distribution was observed, though the range of concentrations was significantly smaller.



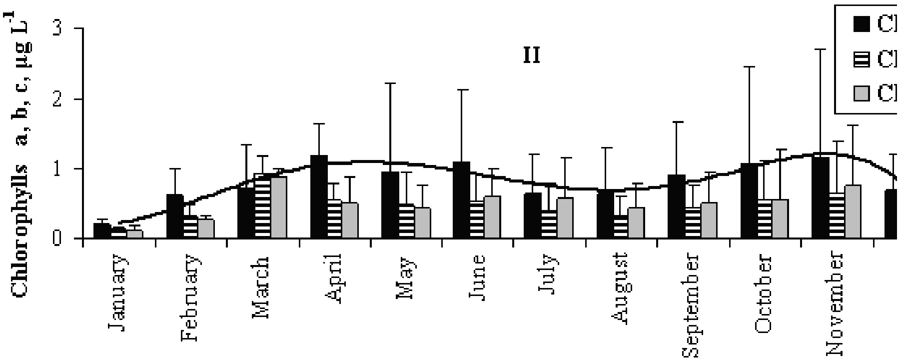


Fig. 9. Chl a, Chl b and Chl c mean monthly concentrations averaged for 2004-2012 in the surface (I) and bottom (II) waters of near the Zmiinyi Island coast

Maximums of Chl *b* average monthly concentrations registered in April and June made respectively 1.28±1.09 µg/l and 1.12±1.94 µg/l and exceeded the minimal values registered in August (0.41±0.43 µg/l) and January (0.19±0.37 µg/l) 3-6 times. Average monthly maximums of Chl *c* were registered in June (0.89±0.90 µg/l) and November (0.85±1.12 µg/l) and exceeded the minimums observed in January (0.23±0.11 µg/l) and August (0.46±0.43 µg/l) 2-4 times.

Seasonal variations of Pheophytin average monthly concentrations (see Fig. 10) practically repeated the seasonal variations of chlorophylls concentrations. Pheophytin maximal concentrations were registered in the surface water layer in April-June (2.29±2.13-1.96±3.02 µg/l), minimal – in January (0.21±0.13 µg/l) and August (0.59±0.90 µg/l). In October the second maximum of Pheophytin *a* concentrations was registered (1.39±2.55 µg/l) being 1.6 times lower than the spring one.

Analysis of Margalef index seasonal variation (see Fig. 11) has shown that changes in its average monthly values take place in opposite phase with Chl *a* concentration variations, which could be proved with negative coefficient of correlation (r=-0.65, p>0.02). Maximal values of Margalef index were registered in January (3.9±0.2) and August (3.5±0.7), the lowest – in April (2.66±0.4). This peculiarity of Margalef index seasonal variation was characteristic of both surface and bottom waters.

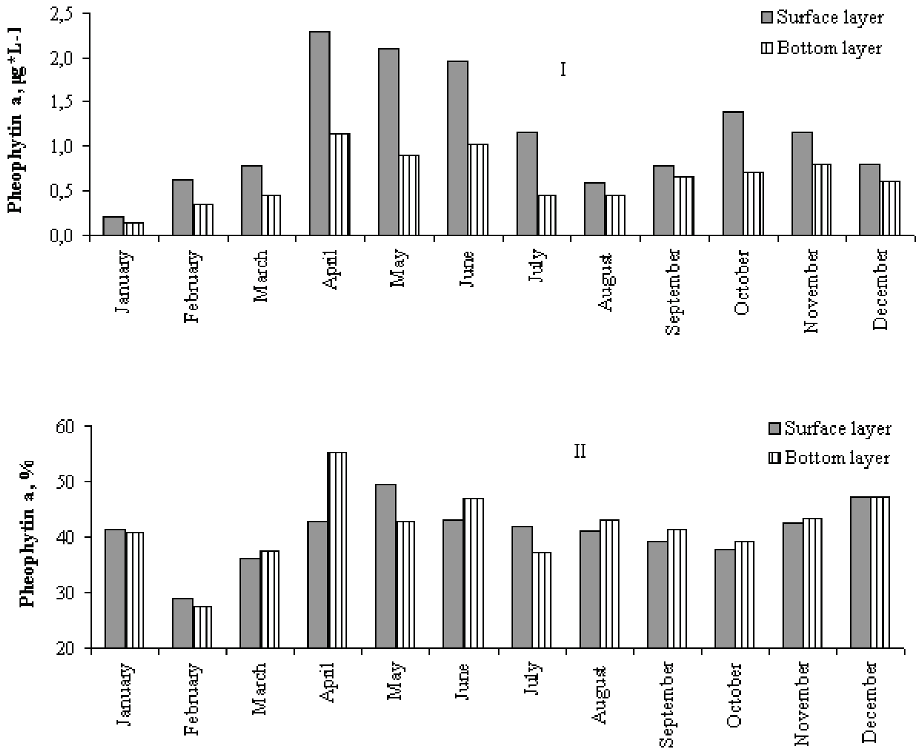


Fig. 10. Averaged for 2004-2012 mean monthly values of absolute and relative concentrations of Pheophytin a in the surface (I) and bottom (II) waters the Zmiinyi Island coast

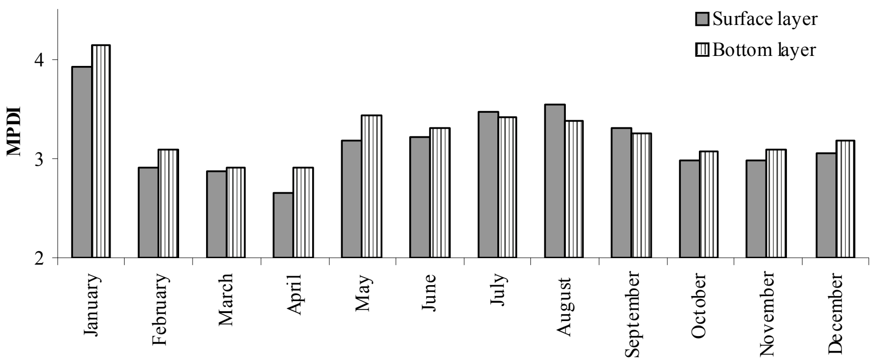


Fig. 11. Averaged for 2004-2012 mean monthly values of MPDI in the surface (I) and bottom (II) waters near the Zmiinyi Island coast

INTER-ANNUAL VARIATIONS

Chlorophylls a, b and c

Inter-annual variation of Chl *a*, Chl *b* and Chl *c* concentrations averaged for vegetation period of each year (May-December) in the surface (I) and bottom (II) waters near the Zmiinyi Island coast according to the data of 2004-2012 are illustrated with Fig. 12. Analysis of Chl *a* concentrations, averaged for a vegetation period (May-December) of each year (from 2004 to 2012), showed that its maximal content in the surface layer (2.52±5.03 μg/l) was observed in 2005. During three years that followed the concentration of Chl *a* decreased almost 2 times. The second maximum of Chl *a* concentration was registered in 2009 (2.05±2.80 μg/l) and then its gradual decrease was observed till the minimal value (0.99±1.08 μg/l) in 2011. Long-term changes analysis has shown a negative trend in distribution of average annual Chl *a* concentrations in 2004-2012.

The same regularities as with Chl *a* were observed with inter-annual variation of Chl *b*, with maximum (1.18±2.42 μg/l) in 2005 and second increase of concentration (0.97±0.99 μg/l) in 2009. Minimal average annual Chl *b* content (0.40±0.37 μg/l) was registered in 2011. Long-term variation of concentrations has also shown a negative trend. As it was shown in [] (Derezyuk & Medinets, 2013), the main characteristics of *Cyanophyceae, Haptophyta, Dictyochophyceae, Heterokontophyta* classes' temporal distribution during 2004-2012 stayed practically at constant level. At that, positive trends of *Bacillariophyta* class have been observed, as well as negative trends of *Dinophyta.* These structural changes in phytoplankton could also be the reason of the PSPs trends observed in the Zmiinyi Island area.

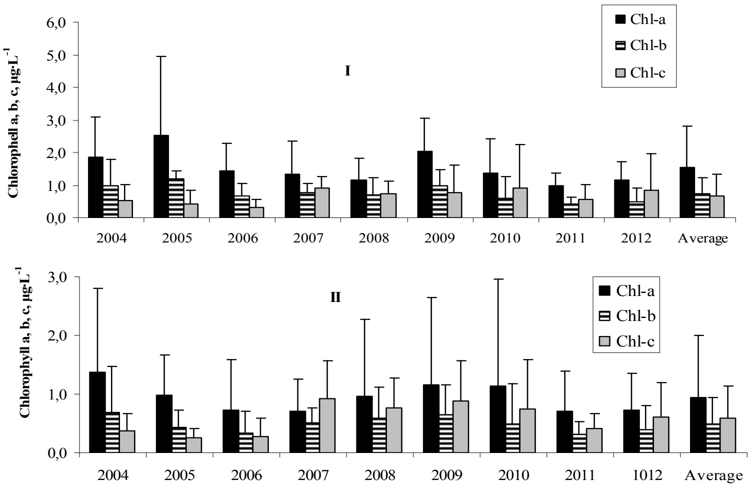


Fig. 12. Inter-annual changes of Chl a, Chl b and Chl c concentrations (vegetation period – May-December) in the surface (I) and bottom (II) marine waters near the Zmiinyi Island coast in 2004-2012

The results of Chl *c* average annual concentrations analysis showed that its maximal content (0.91±1.33 μg/l) happened in 2010 and minimal (0.31±0.24 μg/l) – in 2006. Unlike the long-term changes of Chl *a* and Chl *b* concentrations, a positive trend in concentration was characteristic of Chl *c*: its average annual concentration grew practically 2 times during 9 years.

Pheophytin a and MPDI

Analysis of Pheophytin *a* average annual concentrations distribution (see Fig. 13) shows that the maximum of its concentration (2.61±4.37 μg/l) was observed in 2009 and the minimum in two last years when average annual concentrations made 0.58±0.62 μg/l and 0.79±1.11 μg/l in 2011 and 2012 respectively. At that, changes in Pheophytin *a* concentrations were taking place synchronously with Chl *a* concentrations, which could be proved with significant correlation coefficient ($r=0.70$. $p>0.01$).

Average annual values of MPDI varied within very narrow range from the lowest (2.92±0.48) in 2004 to the highest (3.46±0.96) values in 2006. In 2011 and 2012 Margalef index varied insignificantly and equalled respectively to 3.18±0.54 and 3.17±0.26, which practically coincided with average value of many years' for this parameter.

*Fig. 13. Inter-annual variations of Pheophytin a concentrations (diamonds – absolute (μg*L⁻¹), squares – relative (%)) and MPDI (triangles) in marine surface waters near the Zmiinyi Island during vegetation period (May-December)*

CONCLUSIONS

Analysis of PSPs and Margalef index short-term, seasonal and inter-annual changes study results has shown the following.

1. High changeability of PSPs concentrations was observed in the Zmiinyi Island coastal waters. It has been shown that the values of mean and maximal PSPs concentrations are distributed in the order of decreasing: Chl *a*, Pheophytin *a*, Chl *b*, Chl *c*. Analysis of the concentrations range value (which we determine as the ratio of maximal concentrations to mean ones) has shown that the range in the surface/bottom layer makes: for Chl *a* 17.5/15.6, for Chl *b* 17.8/8.0, for Chl *c* 10.2/8.0, for

Pheophytin *a* 14.8/14.4, and for all the studied characteristics is higher in the surface layer than in the bottom one.

2. Bimodal distribution with spring and autumn maximums was registered in the averaged for 2004-2012 seasonal PSPs variation, which repeated the known distribution of maximums in the Black Sea marine phytoplankton functioning.

3. Analysis of inter-annual changes in PSPs concentrations has revealed negative trends in Chl *a* and Chl *b* distribution and positive trend for Chl *c*, which evidences changes taking place in phytoplankton structure that is proved by the studies of phytoplankton community in the area carried out by other researchers.

4. The unique fact of 2 times' increase of Chl *c* mean concentrations revealed for the years 2004-2012 enables us propose to use the ratio of Chl *c* / Chl *a* concentrations as an indicator of phytoplankton community structural changes, the peculiarities and reasons of which would be the subjects of the further studies.

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РЕЗУЛЬТАТИ ВИВЧЕННЯ ПІГМЕНТІВ ФІТОПЛАНКТОНУ В ПРИБЕРЕЖНИХ ВОДАХ ОСТРОВА ЗМІЇНИЙ В 2004-2012 РР.

Резюме

В роботі детально аналізуються дані за вмістом фотосинтетичних пігментів фітопланктону в прибережних водах острова Зміїний, що отримані в 2004-2012 рр. Представлені результати вивчення сезонних змін і міжрічних трендів вмісту хлорофілу ***а***, хлорофілу ***в***, хлорофілу ***с***, феофітину ***а*** і пігментного індексу Маргалефа. Встановлений факт позитивного тренду хлорофілу ***с***, який може вказувати на структурні зміни у фітопланктонному угрупованні Чорного моря, які відбуваються останніми роками.

Ключові слова: Чорне море, пігменти, хлорофіл, фітопланктон, острів Зміїний.

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РЕЗУЛЬТАТЫ ИЗУЧЕНИЯ ПИГМЕНТОВ ФИТОПЛАНКТОНА В ПРИБРЕЖНЫХ ВОДАХ ОСТРОВА ЗМЕИНЫЙ В 2004-2012 ГГ.

Резюме

В работе подробно анализируются данные по содержанию фотосинтетических пигментов фитопланктона в прибрежных водах острова Змеиный полученные в 2004-2012 гг. Представлены результаты изучения сезонных изменений и межгодовых трендов содержания хлорофилла ***а***, хлорофилла ***в***, хлорофилла ***с***, феофитина ***а*** и пигментного индекса Маргалефа. Установлен факт положительного тренда хлорофилла ***с***, который может указывать на структурные изменения в фитопланктонном сообществе Черного моря, происходящие в последние годы.

Ключевые слова: Черное море, пигменты, хлорофилл, фитопланктон, остров Змеиный.