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ECOLOGY

With the aim to predict shifts in water quality in the Danube river delta, a geographic information system (GIS) for environmental monitoring with additional functions for analyzing time-dependent series of observation results was developed. Using the developed GIS, the main trends of shifts in phycological indices of water quality for the period starting from 2005 were revealed. The topicality of these studies is dictated by the need to determine the impact of shifts in aquatic chemistry on the biotic component of the ecosystem.

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According to data on the Pantle-Buck saprobity index, there was a trend to improving water quality during the study period. A downward trend in species diversity was found using the Shannon diversity index calculated from the abundance of phytoplankton. The revealed trends in phycological indices were observed already in the inlet section of the Danube river delta (above Reni), i.e. they are due to factors operating outside the Danube delta.

The obtained results on the trends of phycological parameters correlate with the previously obtained data of the analysis of the results of monitoring of aquatic chemistry parameters. The revealed downward trend in the saprobity index stems from a trend of improving water quality in terms of: BOD5 (correlation coefficient, R=0.68; significance level, a=6%), phosphate phosphorus (R=0.70; a=5%), suspended solids (R=0.80; a=2%). The downward trend in the Shannon diversity index calculated from the abundance of phytoplankton is explained by an upward trend in manganese concentration (R=-0.75; a=3%).

The decrease in phytoplankton diversity according to the Shannon diversity index calculated from the phytoplankton abundance is explained by a sharp increase in the abundance of cyanophytes.

The results obtained are of significant interest for predicting shifts in the ecological condition of the Danube river delta Keywords: phycological indices, phytoplankton biomass, Shannon diversity index, saprobity index, time-dependent trend

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1. Introduction

The Danube river delta is a unique ecological system. According to the Directive 2000/60/EC of the European Parliament and of the Council dated 23 October 2000 establishing a framework for Community action in the field of water policy (Directive 2000/60/EC) [1], this ecological system refers to water bodies that require special protection. Also, it is noteworthy that the Danube river delta is a transboundary site. The ecological condition of the Danube Delta is determined by both man-made factors acting on the part of the states through whose territories the Danube Delta branches flow, and transboundary factors acting on the part of all European countries whose territories are located within the Danube river basin. Besides, the condition of the Black Sea ecosystem is considered as pre-crisis one, in particular, due to pollution of the Danube river with industrial and municipal wastewaters. Therefore, the assessment of the ecological condition of the Danube river delta is of substanF-----

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GIS-ASSISTED REVEALING OF SPATIO-TEMPORAL DYNAMICS IN PHYCOLOGICAL INDICES OF THE DANUBE RIVER DELTA

A. Vasenko

PhD, Associate Professor, Senior Researcher* E-mail: alexandr.vasenko@gmail.com

> V. Brook PhD, Leading Researcher* E-mail: morlab@ukr.net

Yu. Svyrydov Engineer 3-categories* E-mail: sviridov288@gmail.com

H. Milanich Researcher* E-mail: mypostkeyg@gmail.com *Research Institution "Ukrainian Research Institute of Environmental Problems" Bakulina str., 6, Kharkiv, Ukraine, 61166

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tial interest on both national and international levels. First of all, this relates to the assessment of aquatic chemistry and aquatic biology indices of the Danube mouth branches and predicting shifts in these indices. Integrated assessment and prediction of river water quality are necessary for decision making regarding the environmental safety of the Danube river and the Black Sea.

Studies focusing on water quality in the Danube river before the adoption of the Convention for the Protection of the Danube River in 1994 were performed mainly within individual countries. Taking into account the fact that the Danube basin is an integral system, it was decided to carry out comprehensive monitoring of river waters within its basin. Since 1994, research has been conducted within the framework of the international programme Transnational Monitoring Network (TNMN) under the supervision of the International Commission for the Protection of the Danube River (ICPDR) [2]. At present, monitoring of aquatic chemistry indices of water quality in the Danube river delta is carried out by the Danube Hydrometeorological Observatory (HMO) at monthly intervals. Since 2004, the Ukrainian Research Institute for Environmental Problems (UkrRIEP) periodically conducts additional research on water quality indices. These studies include observations over not only aquatic chemistry, but also phycology. The topicality of additional studies is substantiated by the need to eliminate uncertainties in assessing the impact of various man-made factors on water quality in the Danube.

The most promising seems to be the use of not just an information system, but a geographic information system, which will allow displaying the prediction results visually.

2. Literature review and problem statement

The first qualitative studies of phytoplankton in the Danube river were conducted back in 1898–1899. The results of these studies [3, 4] showed that the species composition of phytoplankton at the end of the 19th century was similar to the modern one, i.e. there was a predominance of diatoms. Later, in the course of studies carried out in the 30s and 40s of the 20th century [5, 6], the predominance of centric diatoms was revealed. In the 1950s, it was shown that in sections of the river where the flow decreases or where eutrophication increases, cyanophytes and green algae can prevail over diatoms, which sometimes leads to the "blooming" of river waters [7]. Similar patterns can be traced in studies conducted in the 2000s [8, 9].

Numerous studies of the modern species composition and quantitative characteristics of the Danube phytoplankton were summarized in [9]. This paper analyzes the spatial and seasonal dynamics of phytoplankton. The study of spatial dynamics was carried out on the basis of an analysis of shifts of chlorophyll *a* in phytoplankton along the river streamway. It was found that the upper and lower reaches of the Danube are characterized by low values of chlorophyll *a* content, and increased and peak values are peculiar to the middle reaches. The increase in chlorophyll a in the middle part of the streamway was repeated in different years of observations. However, the locations of the maximum phytoplankton concentrations and the seasons when the maximums are reached vary. The earliest seasonal maximum was observed in March, the latest one at the end of October. Also, the main hydrophysical indices affecting the shift in phytoplankton biomass were water flow rate in the river and turbidity.

The aquatic biology studies were performed on the freshwater part of the Danube river delta in the course of monitoring studies of the UkrRIEP in the framework of the control over the environmental impact of dredging during the restoration and operation of the Danube – Black Sea deep-water navigational route (DNR) in 2004–2020. Algal samples were taken within the Danube Delta section (0–131 km) at permanent monitoring stations from Reni to the Bystryi arm (0 km) during different seasons of 2005–2020.

During the period 2004–2012, researchers from the Institute of Hydrobiology, the National Academy of Sciences of Ukraine (IHB NASU) carried out multifaceted biological studies of the Danube river delta. The main branches and lagoons in the affected area of the Danube – Black Sea deep-water navigational route were investigated.

The results of phytoplankton studies in the Danube river delta carried out by the UkrRIEP and the IHB NASU [10, 11] showed the following.

The species composition of phytoplankton communities within the Danube estuary area is generally quite diverse. It is more homogeneous in the branches and much richer, with higher indices of quantitative development in lagoons, displaying its sensitivity to local fluctuations in hydrology and aquatic chemistry. The phytoplankton composition of the arms largely depends on the supply of algae from lagoons, in which more favourable conditions are formed for the development of planktonic algal flora, driven by features in hydrology and the development of higher aquatic vegetation. During recent years, a general trend of an increase in the number of species of planktonic algae and a difference in the nature of their seasonal dynamics in lagoons and branches, as well as between individual lagoons, were noted.

In all studied sites, diatoms predominated in all seasons; in warmer seasons, an increase in the proportion of green algae (mainly chlorococcal ones) occurred. The floristic spectrum of phytoplankton was characterized as diatom-chlorococcal (in winter – diatom), against which representatives of other divisions developed more actively in lagoons (in particular, cyanophytes, euglena and golden-brown algae). The values of the Shannon diversity index show the formation of a polydominant complex of planktonic algae species in the studied areas. At the same time, a more significant contribution to the phytoplankton abundance is made by small-celled species (mainly cyanophytes). A more significant contribution to the total biomass is made by large-cell forms (certain species of diatoms, euglena algae and dinoflagellates).

In the dynamics of quantitative indices of planktonic algal flora, significant fluctuations in numbers were observed. Such fluctuations occurred mainly at the expense of smallcell cyanophytes. With more uniform biomass values, the leading role was played by diatoms, typical for river phytoplankton, with a noticeable contribution of cyanophytes and green algae, and in some cases dinoflagellates, golden-brown and yellow-green algae.

During the study period, a slight increase in the total quantitative development of planktonic algae with a significant increase in the role of cyanophytes was registered: in terms of biomass, such an increase was especially evident during the autumn seasons of recent years; in terms of abundance, during all seasons owing to small-celled species, which can be explained by the intensification of eutrophication processes, also observed in previous years.

Despite the general tendency of an increase in the number of planktonic algal species during recent years, the nature of their seasonal dynamics in lagoons differed from that in the branches, as well as from branch to branch and from lagoon to lagoon. This is due to the different stages of succession associated with the unequal species composition, degree and dynamics of overgrowth with higher aquatic vegetation. An exception is the monitoring data for 2011, when there was a consistency of fluctuations in the abundance and biomass of the phytoplankton with the dynamics of species diversity in lagoons.

According to the values of the saprobity index calculated by the Pantle-Buck method, water in most of the sections corresponded mainly to class II, the 3^{rd} category of quality (the values of the saprobity index are in the range of 1.6–2.0: "good" according to the condition of water quality, "sufficiently clean" according to the degree of cleanliness/pollution). Basically, these values of the indices are in the range corresponding to β -mesosaprobic zone, in several cases corresponding to the neighbouring zones: oligosaprobic and α -mesosaprobic ones.

During the periods of low algal vegetation, the classes and categories of water quality of the sections studied, established by the phytoplankton biomass, coincided with those determined by the saprobity index, and in the seasons of active algal proliferation, they significantly decreased to the values corresponding to more polluted zones.

In general, during all years of studies, shifts in the quantitative and qualitative composition of the planktonic algal flora in the examined sections of the Danube river corresponded to the course of the seasonal succession and the type of water bodies examined. Despite the significant variability of the phytoplankton indices from the specific sections, there was a sufficient closeness of the long-run annual averages of the structural and functional characteristics of planktonic algae, which indicates certain stability of the Danube Delta ecosystem.

Correlation analysis of the relationships between various water quality indices in the lower reaches of the Danube river is presented in [12]. On the basis of water quality monitoring data below Galați, Romania, 56 significant correlations were revealed between various water quality indices (the level of significance does not exceed 5 %). In particular, a close positive correlation was found between the concentration of total iron and ammonia nitrogen.

In [13], an analysis of the data of water quality monitoring in the lower reaches of the Danube at 4 observation points, from the mouth of the Siret river, for the period 2013–2016 was reported. Based on these data, a comprehensive assessment of water quality was carried out using the WQI (Water Quality Index). The performed analysis showed that, in general, the worst water quality was observed in August – September, which corresponds to low river flow. However, in some years, the WQI peaks were observed in spring, associated with a volley of pollutants.

In [14], employing statistical methods of principal components and factor analysis, the seasonal dynamics of water quality in the lower reaches of the Danube was analyzed. Three main factors have been identified that affect the seasonal dynamics of water quality: river flow, biological activity of the Danube ecosystem, and human-caused pollution of river water. It is shown that the factor of human-caused pollution makes the greatest contribution in summer.

Phycological parameters were not taken into account in the studies [12–14]. Correlation relationships between aquatic chemistry and phycological indices for the Danube have not been studied. Correlation relationships between aquatic chemistry and phycological indices were analyzed mainly for marine and transitional waters. For example, in [15] for the Red Sea, a multiple correlation between the total abundance of phytoplankton and such aquatic chemistry indices as nitrates, ammonia, silicon oxide, and salinity was investigated. The corresponding multiple regression equation is obtained. In [16], the influence of biogenic elements such as nitrates, ammonium nitrogen, silicon, as well as salinity, pH and dissolved oxygen on phytoplankton of the estuary of the Tapi river, India was studied.

The quantitative phycological indices and the trends of their shifts together with the significance of the trends were not determined in the studies performed. The lack of such results, especially the lack of correlations between phycological and aquatic chemistry parameters, significantly complicates the prediction of shifts in phycological parameters.

3. The aim and objectives of the study

The aim of the study is to assess the spatial and temporal dynamics of phycological indices in the Danube delta for short-term prediction of shifts in them.

To achieve the aim, the following objectives were formulated:

 to carry out quantitative estimations of the average trends in shifts of phycological indices for the research period and assess their significance;

- to investigate correlations between the determined phycological and aquatic chemistry indices.

4. Methodology for phycological studies and analysis of observation time series

Phycological studies included abundance and biomass measurements of the phytoplankton species belonging to the following 8 divisions:

- Cyanophyta cyanophytes;
- Dinoptyta dinoflagellates;
- Cryptophyta cryptophytes;
- Chrysophyta golden-brown algae;
- Xanthophyta yellow-green algae;
- Bacillariophyta diatoms;
- Euglenophyta euglena algae;
- Chlorophyta green algae.

Regular observations were carried out at 13 monitoring stations; their locations are described in [17].

As a rule, the studies were carried out 3 times a year: in April, August and November. Sampling and sample treatment were carried out according to the methods generally accepted in aquatic biology [18]. Based on the measurement results for each month, the following indices were calculated: total phytoplankton biomass, Pantle-Buck saprobity index, Shannon diversity indices for phytoplankton abundance and biomass. For each of the listed indicators, annual averages were calculated.

For a visual presentation of the results of water quality observations, calculations were made using a specially designed Geographic Information System (GIS) for the Danube river delta. The analytical subsystem of the developed GIS included additional units for analyzing monitoring results and specifically a unit for predicting river water quality. The necessity to develop a special GIS is substantiated by the fact that the GIS developed for the Danube river within the framework of the ICPDR project [19], as well as the GIS for environmental monitoring of surface water quality used by the State Water Agency [20] lack some important functions for data analysis. First of all, this concerns the functions that allow identifying trends in aquatic chemistry and phycological parameters. In addition, there are no functions that allow assessing the correlations between various aquatic chemistry and phycological indices, performing a comprehensive assessment of water quality and predicting its shift.

To predict the values of individual and integrated indices of river water quality for a certain period of time, the prediction unit provides for the use of various methods of exponential smoothing. The choice of a particular predicting method depends on the presence or absence of a time-dependent trend in the predicted index. Therefore, at the first stage of predicting, the temporal trend of the index is calculated and its significance is determined. Due to the small number of points in the analyzed time series (n=11), the one-tailed Student's *t*-test was applied to calculate the magnitude and direction of the trend and assess its significance. According to this technique, the time-dependent trend a_1 is calculated as the coefficient of the independent variable in the linear regression equation. The calculation technique is described in [17].

If a significant trend in the temporal variation of the index is not identified, the method of simple exponential smoothing is used for predicting. Otherwise, the Holt procedure or the Holt-Winters procedure is used for predicting. The Holt procedure is used to predict the annual averages of indices; and the Holt-Winters procedure for predicting monthly or quarterly averages (taking into account seasonal indices).

5. Results of time series analysis in phycological observations

Annual averages of phycological indices, averaged over the monitoring stations, as well as calculated values of time-dependent trends and their significance levels are presented in Table 1.

Annual average values of phycological indices, averaged over the monitoring stations

Table 1

	1				
	Phycological indices				
Observation year	Phyto- plankton biomass, mg/dm ³	Pan- tle-Buck saprobity index	Shannon diversity index for abundance, bit/cell	Shannon diversity index for biomass, bit/mg	
2005	1.52	2.01	3.33	3.04	
2007	1.42	1.87	2.49	2.48	
2008	3.70	1.54	2.76	2.92	
2009	1.30	1.78	4.06	3.27	
2010	4.28	1.86	2.39	3.40	
2011	1.82	1.70	2.87	2.56	
2013	1.75	1.34	1.94	3.14	
2014	2.18	1.62	1.74	4.07	
2015	3.30	1.63	2.33	3.30	
2016	2.57	1.63	1.79	3.06	
2017	1.82	1.63	2.19	3.91	
Long-term annual average	2.33	1.69	2.54	3.20	
Time-dependent trend	0.032	-0.028	-0.119	0.070	
Significance level of the trend	0.72	0.05	0.02	0.07	

Curves of temporal dynamics of annual averages of phycological indices are plotted in Fig. 1.

As can be seen from the data tabulated in Table 1, on average for the Danube river delta during the study period, there was a slight improvement in water quality according to the saprobity index. At the same time, there was a slight increase in the Shannon diversity index calculated for phytoplankton biomass, and a certain decrease in the Shannon diversity index calculated for phytoplankton abundance. No significant shifts in total phytoplankton biomass were observed. A significant (by 40 %) decrease in the Shannon index for phytoplankton abundance indicates a deterioration in the ecological condition of water in the Danube river delta. The average value of phytoplankton biomass over the observation period is 2.33 mg/dm^3 . According to the ecological classification used [21], this value corresponds to the 4th category of water quality ("slightly polluted"). The average value of the saprobity index (1.69) corresponds to the 3rd category of water quality ("sufficiently clean").

As can be seen in Fig. 1 (curve 3), a significant decrease in the Shannon diversity index for abundance was observed starting from about 2013.

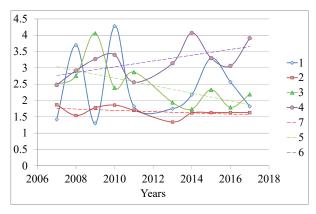


Fig. 1. Curves of temporal dynamics of average annual values of phycolological indices: 1 - phytoplankton biomass, mg/dm³; 2 - Pantle-Buck saprobity index; 3 - Shannon diversity index for abundance, bit/cell; 4 - Shannon diversity index for biomass, bit/mg; 5 - Pantle-Buck saprobity index (linear trend);
6 - Shannon diversity index for abundance (linear trend);
7 - Shannon diversity index for biomass (linear trend)

In order to identify the reasons for changes in the indices of phytoplankton diversity, the trends in the abundance and biomass of various phytoplankton divisions were calculated. The calculation results are shown in Table 2.

Table 2

Time-dependent trends in abundance and biomass of various algal groups

Algal groups	Abundance		Biomass	
	Trend	Significance level	Trend	Significance level
Cyanophyta	3.60	0.001	0.048	0.02
Dinophyta	-0.0008	0.12	-0.0029	0.14
Cryptophyta	0.0055	0.11	-0.0009	0.7
Chrysophyta	0.28	0.008	0.025	0.01
Xanthophyta	-0.26	0.33	-0.059	0.285
Bacillariophyta	-0.021	0.77	-0.372	0.92
Euglenophyta	0.0043	0.31	-0.0008	0.77
Chlorophyta	0.040	0.75	0.0078	0.58

As can be seen from Table 2, significant positive trends were observed only for 2 divisions: cyanophytes and golden-brown algae. Curves of the abundance of phytoplankton belonging to these divisions of algae by the years of study are plotted in Fig. 2.

As can be seen from the curves presented, a significant increase in the phytoplankton abundance for these divisions was observed starting from 2013. A similar picture is observed for the biomass of cyanophytes and golden-brown algae.

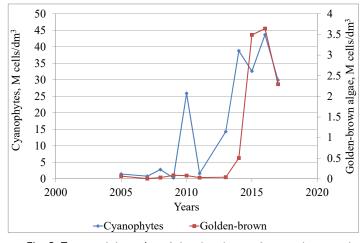


Fig. 2. Temporal dynamics of the abundance of cyanophytes and golden-brown algae

6. Results of correlation analyses of relationships between phycological indices and aquatic chemistry parameters

The revealed correlation coefficients between the saprobity index and aquatic chemistry parameters, which usually affect this phycological index (concentrations of biogenic and organic substances), are tabulated in Table 3.

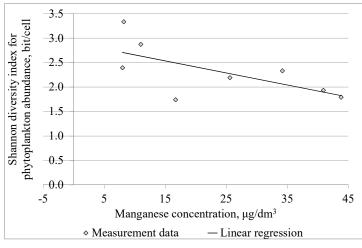
Correlation coefficients between the saprobity index and concentrations of biogenic and organic substances

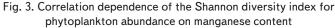
Table 3

Indices	BOD_5	COD	Ammonium nitrogen	Nitrite nitrogen	Phosphate phosphorus
Correlation coefficients	0.68	0.52	0.48	0.11	0.70
Significance levels, %	6	19	22	80	5

Moreover, a close positive correlation was found between the saprobity index and the concentration of suspended solids: correlation coefficient, R=80; significance level, $\alpha=2$ %.

As to the Shannon diversity index calculated for phytoplankton abundance, a significant negative correlation dependence on the concentration of manganese was found (Fig. 3).





The remarkable thing is that in 2013, a sharp increase in the concentration of manganese was observed. If until 2013 the concentration of manganese was at the level of commercial fishing MPC, then since 2013 this fishing standard has been exceeded by about 3 times. The correlation coefficient, *R*, of the relationship between the Shannon diversity index, calculated from the abundance of phytoplankton, and the concentration of manganese, is -0.75, the significance level, α , is 3 %.

7. Discussion of the identified trends in indices and correlation dependences

The obtained results on the trends of phycological indices correlate with the analytical data of the results of aquatic chemistry monitoring [22]. It can be assumed that the revealed trend toward a

decrease in the saprobity index is due to the trend revealed in [17] towards improving water quality in terms of indices featuring organic substance content (BOD₅ and COD), the content of biogenic substances (ammonia nitrogen, nitrite nitrogen, phosphate phosphorus), as well as suspended solids. However, as can be seen from the data given in the previous section (Table 3), significant correlations were established for the dependence of the saprobity index only on 3 indices as follows: suspended solids, BOD₅ and phosphate phosphorus. With that in mind, it can be concluded that the decrease in the saprobity index is primarily due to a decrease in the intake of phosphates and biologically oxidized organic substances originating from domestic wastewater discharged into the river waters of the Danube river basin.

The observed trend towards a decrease in the Shannon diversity index, calculated from the abundance of phytoplankton, is probably caused by the trend towards an increase in the concentration of manganese revealed in [17].

All identified trends in phycological indices were observed already in the inlet section of the Danube river delta (monitoring station R01), that is, they are caused by factors acting outside the study area.

It is remarkable fact that starting from 2013, when a sharp increase in the concentration of manganese and, at the same time, a sharp decrease in the Shannon diversity index

> for phytoplankton abundance were observed, the ratio between the concentrations of manganese and zinc in river waters shifts. If until 2013 the concentration of zinc was higher than the concentration of manganese, then since 2013 the concentration of manganese already exceeds the concentration of zinc. This is consistent with the results obtained in [22] for water bodies of Moldova regarding the influence of the ratio between the concentrations of metals on the abundance of phytoplankton. However, the question of the causal relationship between an increase in manganese concentration and a decrease in the Shannon diversity index for phytoplankton abundance requires additional research.

> The influence of manganese on phytoplankton is ambiguous. According to the data given in [22], the stimulating effect of manganese is manifested at concentrations up to 50 μ g/dm³, and the inhibitory effect at concentrations exceeding 300 μ g/dm³. However, according to [23], the inhibitory effect

of manganese is manifested at concentrations even slightly exceeding the commercial fishing maximum permissible concentration (10 μ g/dm³).

As can be seen from the diagrams of the share of different algal groups in phytoplankton abundance (Fig. 4, 5), an increase in the share of golden-brown algae did not significant-

ly affect the Shannon index. At the same time, an increase in the share of cyanophytes led to a significant decrease in diversity due to the overwhelming predominance of cyanophytes. On the contrary, an increase in the biomass of cyanophytes led to an increase in diversity according to the Shannon index for biomass. This is clearly seen from the diagrams of the share of different algal groups in phytoplankton biomass (Fig. 6, 7). In this case, the increase in biodiversity is a consequence of the leveling of the overwhelming predominance of diatoms.

Thus, the decrease in the phytoplankton species diversity is explained by the stimulating effect of manganese concentration on the abundance of cyanophytes.

It is important that previously investigations to identify trends in the diversity of phytoplankton and their dependence on aquatic chemistry parameters for the Danube river delta were not carried out. All revealed tendencies manifested themselves already in the inlet section of the Danube delta, and, therefore, are conditioned by factors acting outside the study area. It is of interest to conduct additional studies on other rivers, as well as laboratory studies, in order to clarify the question whether the results obtained are of a regional or general nature.

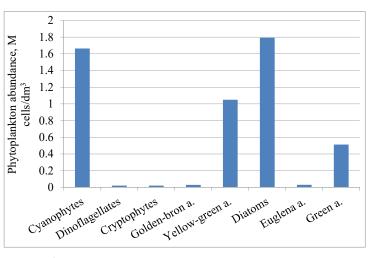


Fig. 4. Share of different algal groups in phytoplankton abundance according to observation data for 2011

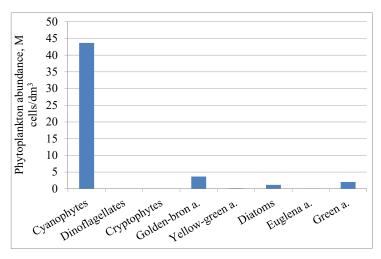


Fig. 5. Share of different algal groups in phytoplankton abundance according to observation data for 2016

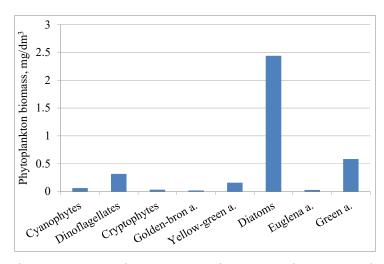


Fig. 6. Share of different algal groups in phytoplankton biomass according to observation data for 2011

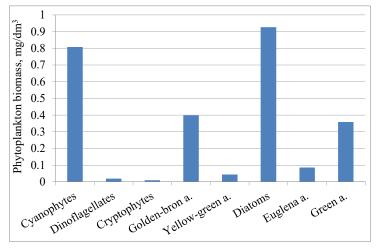


Fig. 7. Share of different algal groups in phytoplankton biomass according to observation data for 2016

7. Conclusions

1. Average trends in the following phycological indices were revealed: Pantle-Buck saprobity index (-0.028 units/year), Shannon diversity index for phytoplankton abundance (-0.119 bit/cell/year), Shannon diversity index for phytoplankton biomass (0.007 bit/mg/year). The signifi-

cance levels of the revealed average trends for all phycological parameters, except for the Shannon index for biomass, did not exceed 5 %. The significance level of the trend in the Shannon index for biomass was 7 %. A decrease in the saprobity index indicates an improvement in water quality in terms of indices featuring the pollution of river water with organic and biogenic substances. A decrease in the Shannon diversity index for phytoplankton abundance indicates deterioration in the ecological condition of river waters due to the intensive development of cyanophytes.

2. Correlation relationships between shifts in phycological and aquatic chemistry parameters were established. For the saprobity index, significant correlation relationships were established with the following indices: suspended solids (correlation coefficient, R=0.80; significance level, $\alpha=2$ %), phosphate phosphorus (R=0.70; $\alpha=5$ %), BOD₅ (R=0.68; $\alpha=6$ %). The revealed negative

correlation between the concentration of manganese and the Shannon index for phytoplankton abundance is of greatest interest. The correlation coefficient is -0.75 (significance level, $\alpha=3$ %). It was shown that the negative effect of manganese on the diversity of phytoplankton is caused by the intensive development of cyanophytes owing to the stimulating effect of high concentrations of manganese.

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