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ANALYSIS OF THE CONTENT OF HEAVY METALS IN PHYTOPLANKTON OF THE ZAPORIZHIA RESERVOIR

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The aim: *to investigate the features of the distribution and accumulation of heavy metals by phytoplankton in different parts of the Zaporizhia reservoir.*
Materials and methods. *Phytoplankton samples were collected in the summer of 2019 at 5 sites along the watercourse of the Zaporizhia reservoir. The concentration of heavy metals in the samples was determined using the C115-M1 atomic absorption spectrophotometer, at specific wavelengths corresponding to the maximum absorption of each of the studied metals in accordance with standard methods. The metal content was expressed in mg/kg dry weight. Statistical processing of the obtained data was carried out according to generally accepted methods using the "Microsoft Excel 2010" software.*
Results. *Studies have revealed that the maximum content of Pb, Zn, Cu, Ni, Fe is recorded in the phytoplankton of the creek of the Mokra Sura river; the maximum content of Mn is revealed on the Monastyrsky island, and the content of Cd is the largest in phytoplankton of the lower part of the reservoir. It has been found that the bioconcentration factors of Iron and Magnesium in phytoplankton are characterized as ultrahigh at all the studied points; those of Nickel, Zinc and Copper are characterized as high. Lead and Cadmium bioconcentration factors can be characterized as moderate at most sampling points; however, they are high at the lower part of reservoir.*
Conclusions. *The content of heavy metals in phytoplankton in different parts of the Zaporizhia reservoir differs significantly. Phytoplankton of the Zaporizhia reservoir is able to accumulate heavy metals, especially Iron and Magnesium, which are accumulated in large amounts; the maximum indicators of these elements are recorded in the Samara bay. There is a difference between absolute concentrations of heavy metals in phytoplankton and its accumulative capacity. It is related to both the hydrological and hydrochemical conditions of the area and the qualitative and quantitative composition of phytoplankton*
Keywords: *phytoplankton, heavy metals, Zaporizhia reservoir, accumulation coefficients*

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1. Introduction

Heavy metals are among the priority pollutants of the hydrosphere, especially continental water bodies, which include the Zaporizhia reservoir – one of the most anthropogenically loaded in the entire cascade of reservoirs located on the Dnipro river [1–3].

The main sources of heavy metals in the reservoir are industrial wastewater, precipitation, small rivers of the Dnieper basin, as well as bottom sediments, which under certain conditions can become a source of secondary pollution of water masses with heavy metals [2, 4]. Landscape geochemical transformations that occur in the catchment area of the reservoir, as well as high toxicity of relatively low concentrations of heavy metals in combination with their ability to bioaccumulate and biomagnification cause toxic risk zones [2, 5].

Assessment of the toxicity of heavy metals in the aquatic environment is a necessary condition for the ecological assessment of aquatic ecosystems and potential risks to human health [6]. However, to determine the degree of impact of heavy metals on aquatic organisms, it is necessary to know their content, patterns of entry, accumulation and distribution in aquatic organisms. A special role in these processes is given to phytoplankton, which includes available forms of heavy metals in biochemical cycles, promotes their transition from ionic to mineral forms and adsorbs metal compounds on the cell membrane or mucus [7, 8]. The ability of algae to actively concentrate heavy metals can have a significant environmental impact: the risk of accumulation of toxicants in photosynthetic cells and their transition to food chains increases [9–11].

2. Literature review

The problem of pollution of aquatic ecosystems with heavy metals is one of the first in terms of ecological significance [12, 13]. The biological consequences of heavy metal pollution of the environment are manifested primarily in the direct toxic effect on aquatic organisms, which leads to the destruction of their physiological systems and the mass death of organisms [14, 15]. In addition, there is a violation of primary products and trophic relationships, as well as the balance between auto- and heterotrophic organisms, which leads to disruption of the biotic cycle and destabilization of aquatic ecosystems [1, 11].

There is a significant amount of articles in the literature on the accumulation of heavy metals by different groups of aquatic organisms (crustaceans [16], molluscs [2, 7], fishes [17], higher plants [4]), but due to the difficulty of sampling very little attention is paid to phytoplankton. Most of the available work on the accumulation of heavy metals phytoplankton was carried out in the laboratory on individual crops and cannot take into account the full range of factors operating in the natural hydroecosystem [6, 9, 10].

However, planktonic organisms should be considered as the most important links in the food chains of water bodies, which play a huge role in the concentration and biogenic migration of metals [12]. Thus, the concentrations of heavy metals largely determine their effect on the variability of the structure of phytoplankton. When reaching concentrations that inhibit the physiological processes of aquatic plant organisms, heavy metals can be considered as a factor that can affect the value of the structural parameters of phytoplankton groups [9, 19]. In the case of multiple manifestations of the limiting effect during the annual cycle, the metal can affect the interannual variability of structural indicators, thereby disturbing the ecological balance of the hydroecosystem [14, 19].

3. The aim and objectives of the study

The aim of the work is to study the peculiarities of distribution and accumulation of heavy metals by phytoplankton in different parts of the Zaporizhia Reservoir.

To achieve this goal, the following tasks were set:

1) to determine the content of heavy metals in the phytoplankton of the Zaporizhia reservoir;

2) to determine the coefficients of accumulation of heavy metals in different parts of the Zaporizhia reservoir;

3) to establish priority metals pollutants in different parts of the Zaporizhia reservoir and possible reasons for their accumulation.

4. Materials and methods

Phytoplankton samples were taken by Apstein plankton mesh (gas No. 77), in the surface layer of water (0.5 m), in the summer of 2019 in 5 areas along the Zaporizhia reservoir, which differ in hydrological and hydrochemical conditions (Fig. 1): Samara bay, Festival berth, Monastyrsky island, the mouth of the Mokra Sura river and the lower part of the reservoir (Viyskove village).

In preparation for the analysis, the phytoplankton was homogenized, dried at 105 °C to constant weight, and then incinerated at 450 °C to obtain a white ash, which was treated with 1N nitric and 1N hydrochloric acid. The resulting solution was filtered through a blue tape filter and transferred to a container up to 10 ml.

The concentration of heavy metals in the samples was determined on an atomic absorption spectrophotometer C115-M1, at appropriate wavelengths corresponding to the maximum absorption of each of the investigated metals according to standard methods. The metal content was expressed in mg / kg dry weight [20, 21].

The obtained data were subjected to mathematical processing by generally accepted methods of variation statistics using application packages Microsoft Excel-2010. Evaluation of the probability of the difference between mean and relative values was performed using Student's t-test at a significance level of $p \le 0.05$.

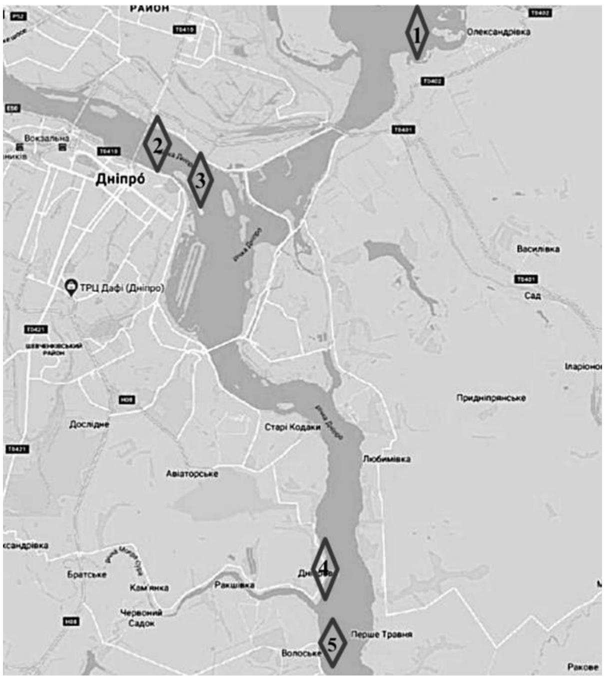

Fig. 1. Layout of sampling points:
1 – Samara bay; 2 – Festival berth;
3 – Monastyrsky island;
4 – the mouth of the Mokra Sura river;
5 – the lower part of the reservoir (Viyskove village)

5. Research results

During the study period, the phytoplankton of the Zaporizhia reservoir was represented by 35 species and intraspecific taxa belonging to 5 divisions: Chlorophyta (13), Bacillariophyta (12), Cyanophyta (8), Euglenophyta (1) Chrysophyta (1). The greatest taxonomic diversity (27 v.v.t.) is recorded in the lower part of the reservoir, the minimum - in the Samara bay (13 v.v.t.).

At all sampling points, the basis of abundance (85–98 %) and biomass (30–70 % (Fig. 2)) was formed by representatives of Cyanophyta, in particular the genus Microcystis. The maximum values are recorded in the Samara bay, and the minimum in the lower part of the reservoir. It was found [6] that algae of this genus are highly sensitive to various contaminants, including heavy metals.

Among the heavy metals that have a significant impact on the hydroecosystem of the Zaporizhia reservoir, we should highlight: lead, cadmium, zinc, copper, iron, manganese, nickel [2].

Studies have shown that the content of heavy metals in phytoplankton in different parts of the Zaporizhia reservoir differs significantly (Fig. 3). Thus, the maximum concentration of lead is recorded at the mouth of the Mokra Sura river and exceeds that in other areas by 10–52 %.

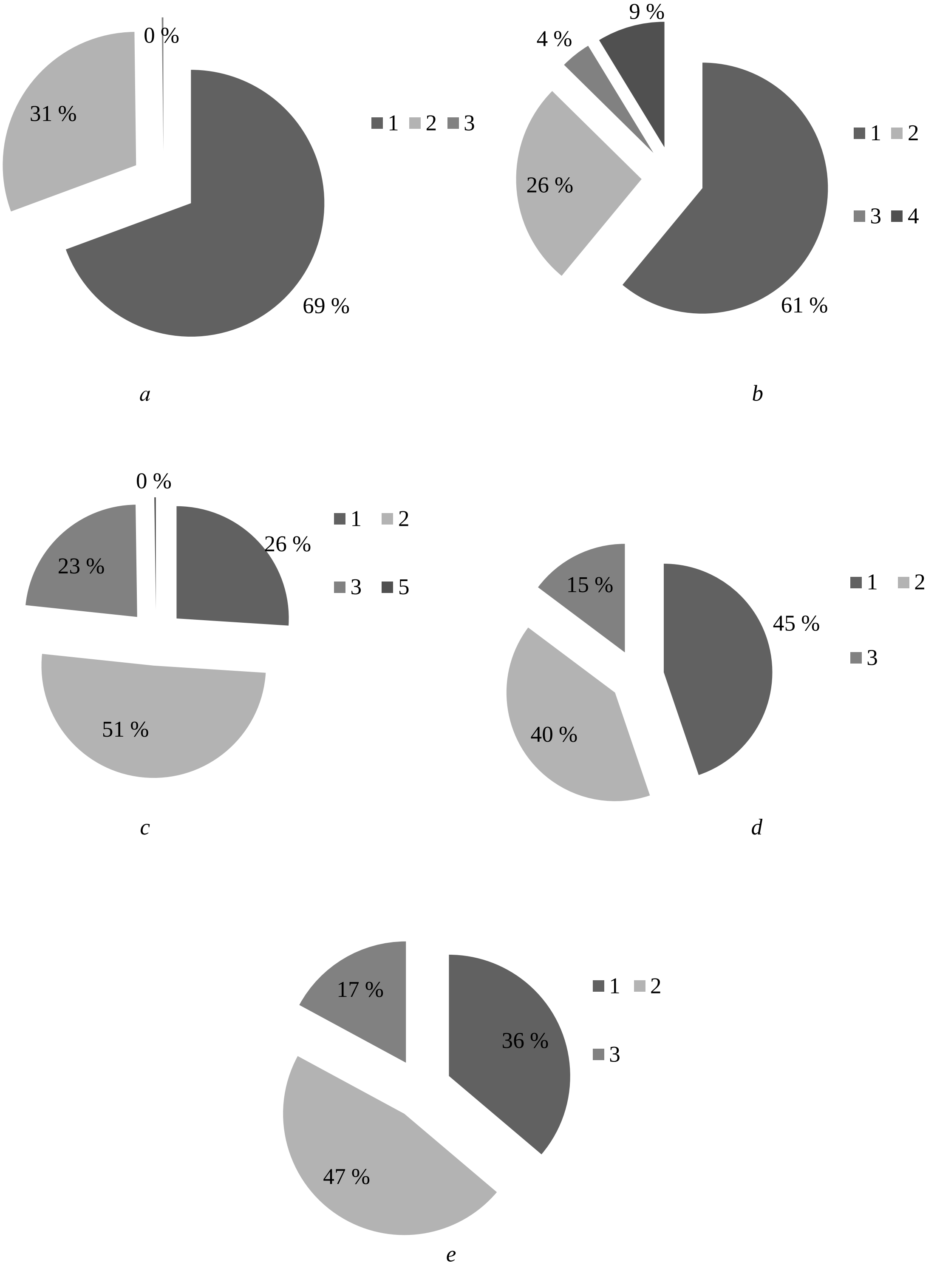

Fig. 2. Distribution of phytoplankton biomass in different parts of the Zaporizhia reservoir:
a – Samara bay; *b* – Festival berth; *c* – Monastyrsky island; *d* – the mouth of the Mokra Sura river; *e* – the lower part of the reservoir (Viyskove village);
1– Cyanophyta ; 2 – Chlorophyta; 3– Bacillariophyta; 4– Euglenophyta; 5–Chrysophyta

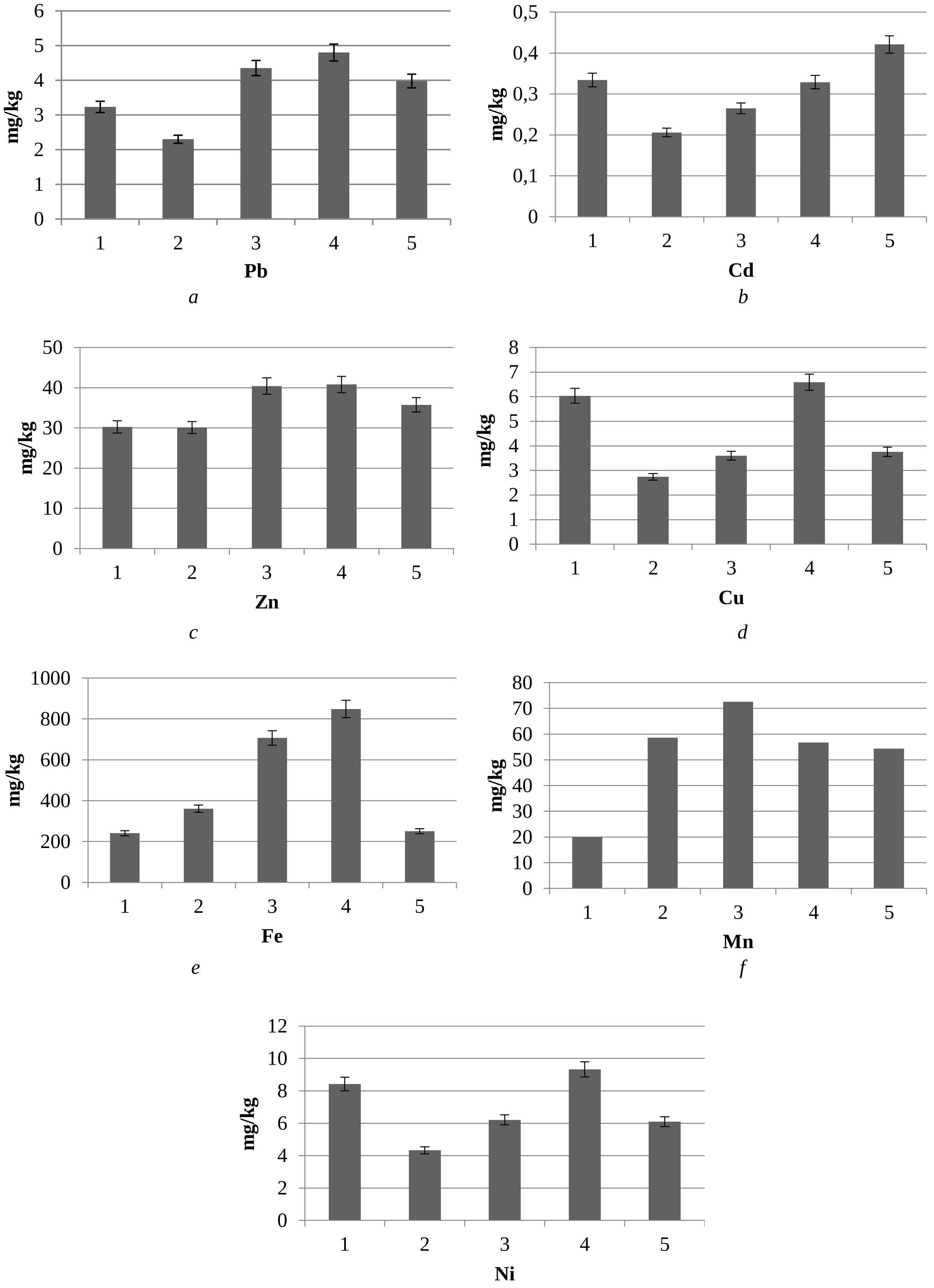

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Fig. 3. The content of heavy metals in phytoplankton in different parts of the Zaporizhia reservoir:
a – The content of Pb; *b* – The content of Cd; *c* – The content of Zn; *d* – The content of Cu;
e – The content of Fe ; *f* – The content of Mn; *g* – The content of Ni;
1 – Samara bay; 2 – Festival berth; 3 – Monastyrsky island; 4 – the mouth of the Mokra Sura river; 5 – the lower part of the reservoir (Viyskove village)

The highest concentration of cadmium in the phytoplankton of the Zaporizhia reservoir was found in the lower part of the reservoir, which is 21–49 % higher than at other sampling points. Slightly smaller fluctuations were observed in the zinc content, so the maximum concentration in the phytoplankton of the mouth of the Mokra Sura river was only 20 % higher than the minimum in the area of the Festival berth. Significant differences were observed in the content of copper and iron - from 8 to 60 % and 17–72 %, respectively. The highest absolute concentration of which is recorded in the phytoplankton of the mouth of the river Mokra Sura.

The maximum content of manganese was found in the phytoplankton of Monastyrsky island, which is 72 % higher than in Samara bay, where the lowest content was recorded. As for nickel, its highest absolute concentration in the phytoplankton of the mouth of the Mokra Sura river exceeds the lowest in the area of the Festival berth by 50 %.

To determine the impact of heavy metals on organisms and quantify the level of bioaccumulation, the coefficient of biological accumulation is determined - the ratio between the metal content in the body and the environment (Table 1) [7, 15].

Table 1

Average values of phytoplankton accumulation coefficients of heavy metals of Zaporizhia reservoir

Selection point	Pb	Cd	Zn	Cu	Fe	Mn	Ni
Samara bay	50.47	30.36	275.09	355.00	6011.25	1668.33	210.50
Festival berth	85.19	103.00	250.92	304.44	2123.29	1222.50	360.83
Monastyrsky island	63.97	115.22	269.47	300.00	2618.11	1370.38	194.06
The mouth of the Mokra Sura river	65.75	102.81	268.49	366.11	2737.77	1290.00	207.33
The lower part of the reservoir (Viyskove village)	248.75	300.71	558.44	341.82	1318.63	1325.37	435.71

6. Discussion of research results

For most of the studied metals (Pb, Zn, Cu, Fe, Ni) in phytoplankton, the maximum content was found in the mouth of the Mokra Sura river, which is probably due to the inefficient operation of right-bank sewage treatment plants and the influence of the Mokra Sura river in which is discharged by wastewater from a number of enterprises in Dnipro, as well as local residents.

According to the classification of K. Vrochinsky at all studied points, the coefficients of accumulation of iron and manganese phytoplankton were characterized as ultrahigh; nickel, zinc and copper are high. The accumulation coefficients of lead and cadmium at most sampling points were characterized as moderate, only at the lower part of the reservoir – as high.

The maximum recorded values of the accumulation coefficient are explained by the high biological activity of iron, which to some extent affects the intensity of phytoplankton development and the qualitative composition of the microflora in the reservoir [19, 22].

In addition, the growth of iron and manganese is facilitated by poor infiltration conditions due to poorly permeable layers, low water filtration rate, high metal content in the mineral composition of rocks, the presence of organic matter, acid reaction, the presence of humic acids, carbon dioxide and oxygen , which is more pronounced in the Samara bay [11, 19].

High values of accumulation coefficients of copper, nickel and zinc by phytoplankton, at their high concentrations in water, indicate the presence of sources of local pollution of natural waters with toxic compounds, especially in the mouth of the Mokra Sura river (copper) and the lower part of reservoir (zinc and nickel) [2, 9].

In the area of the Viyskove village was noted the high accumulative capacity of phytoplankton in relation to lead, cadmium, zinc and nickel, due to favourable hydrological and hydrochemical regime, leaching of metals downstream and higher compared to other points of biodiversity of phytoplankton [5]. The latter contributes to the self-cleaning of the reservoir from toxic metal com pounds [9]. In addition, it should be borne in mind that zinc is a biogenic metal, zinc ions are involved in key reactions of photosynthesis, it is actively absorbed by phytohydrobionts with the onset of the growing season [4, 14].

Average coefficients of accumulation of heavy metals by phytoplankton of the Zaporizhia reservoir allow to place the investigated metals in such sequence on disposal:

1) Samara bay: Fe>Mn>Cu>Zn>Ni>Pb>Cd;
2) Festival berth: Fe>Mn>Ni>Cu>Zn>Cd>Pb;
3) Monastyrsky island: Fe>Mn>Cu>Zn>Ni>Cd>Pb;
4) The mouth of the Mokra Sura river: Fe>Mn>Cu>Zn>Ni>Cd>Pb;
5) The lower part of the reservoir (Viyskove village): Mn>Fe>Zn>Ni>Cu>Cd>Pb.

Study limitations. It should be noted that this study was limited to the summer period, when there was a "bloom" of the reservoir, and the concentration of phytoplankton reached maximum values.

Prospects for further researches. The presented research results are the initial link in the study of the peculiarities of accumulation and distribution of heavy metals in the phytoplankton of the Zaporizhia reservoir and require further detailed study in the dynamics.

6. Conclusions

1. The content of heavy metals in phytoplankton in different parts of the Zaporizhia reservoir differs significantly, so for most of the studied metals, the worst indicators were characterized by phytoplankton at the mouth of the Mokra Sura river, due to the impact of right-bank sewage treatment plants and Mokra Sura river, carrying industrial and domestic effluents.

2. Phytoplankton of the Zaporizhia reservoir is able to accumulate heavy metals, especially iron and manganese, the maximum values of which are recorded in the gulf of

Samara, which leads to a decrease in their concentrations in the water, i.e. self-cleaning of the reservoir.

High coefficients of accumulation of lead, cadmium, zinc and nickel by phytoplankton were observed in the lower part of the reservoir, and copper - in the mouth of the Mokra Sura river.

3. Differences in concentrations and accumulation coefficients in different parts of the reservoir indicate a peculiar complex of hydrochemical and hydrological conditions, differences in the qualitative and quantitative composition of phytoplankton, and the presence of local sources of pollution of natural waters with toxic compounds.

Conflicts of interest

The authors declare that they have no conflicts of interest.

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