Evaluation of the Seasonal Variability of Nutrient in Water of Kuibyshev Reservoir

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Abstract. On the basis of generalization and analysis of long-term data, the peculiarities of the processes of pollution by nutrients of the waters of the Kuibyshev reservoir were studied and the specificity of the seasonal variability of nutrients was revealed. It was revealed that all the nutrients in the water of the Kuibyshev reservoir are characterized by seasonal variability, which is most pronounced in nitrate ions. The results of the study show that in 2009-2015 yrs perennial average monthly concentrations of nutrients did not exceed the fishery standards in the water of the Kuibyshev reservoir.

1. Introduction
The Kuibyshev reservoir is a multipurpose reservoir that provides seasonal regulation of the flow of the Volga river. The reservoir is used in the interests of a number of sectors of the economy: industry and energy, drinking and domestic water supply, health care, agriculture, fish, forestry and hunting, mining, transport, recreation, construction, fire safety, etc. [1, 2].

The water quality of the Kuibyshev reservoir is formed under the influence of transit transport of pollutants from overlying subjects of the Russian Federation, as well as due to discharges of insufficiently treated wastewater from industrial and public utilities and surface runoff from an urban area [3].

In recent years, the rates of silting and “flowering” of the waters of the Kuibyshev reservoir, caused by the processes of eutrophication, have increased many times. Eutrophication is an increase in the biological productivity of water bodies as a result of the accumulation of biogenic elements in water under the action of natural or anthropogenic factors. The main driving force behind the processes of eutrophication of water bodies are biogenous elements (nitrogen and phosphorus compounds). Excessive amounts of biogenic elements trigger the processes of excessive growth of aquatic vegetation and the deterioration of water quality [4].

The main anthropogenic sources polluting the biogenous elements of the Kuibyshev Reservoir are organized sources (industrial and utility discharges), as well as unorganized (diffuse) sources (livestock farms, agricultural land, surface runoff from urbanized areas) [5, 6].

The study of the variability of nutrients is important for assessing the state of aquatic ecosystems. In this article, on the basis of generalization and analysis of long-term data, identify patterns of seasonal dynamics of nutrients in the water of the Kuibyshev reservoir, which will reveal the specifics
of changes in the trophic conditions of the reservoir ecosystem during the seasons of the year, assess
the supply of nutrients in the water column of the reservoir as during winter low water, and spring
flood.

This article is a continuation of a series of works by the authors [7 - 9] devoted to the assessment of
pollution by nutrients of the waters of the Kuibyshev reservoir and the assessment of the nutrient load
on the reservoir catchment within the Republic of Tatarstan.

2. Materials and methods
As source materials, systematic observations of the Federal state budgetary institution «Sredvolgavodkhoz» on the pollution of the water of the Kuibyshev reservoir for the period from 2009 to 2015 yrs were used.

Ammonium ions, nitrate ions, nitrite ions, phosphate ions were considered as biogenic substances. According to the results of hydrochemical analysis of water samples for nutrients, perennial average monthly concentrations in maximum permissible concentration (MPC) of fishery value for 2009-2015 yrs in the whole of the Kuibyshev reservoir.

In order to obtain comparable information, the processing of observations of the pollution of the waters of the Kuibyshev reservoir was carried out using the normative and methodological documents used in the monitoring system of Roshydromet and physical and statistical analysis methods given in [10, 11].

3. Results and discussion

Ammonium ions. The main source of ammonium ions in surface waters are organized (discharges of industrial enterprises, enterprises of housing and communal services) and diffuse sources (surface runoff from the catchment area, including from agricultural land, territories of settlements, from livestock farms, etc.) [5].

Seasonal changes in the concentration of nitrogen in its various forms in small and medium-sized rivers are significantly dependent on the intrawatering nitrification-denitrification processes. According to [12 ], the main regularity of the intra-annual course of nitrogen-containing substances is the presence of their maximum content in the spring, which is primarily due to the flushing of these substances from the catchment area; their minimum concentrations occur in the summer period (in the reservoirs of Russia), which is associated with their active absorption by hydrobionts.

Seasonal variability of perennial average monthly concentrations of ammonium ions in the water of the Kuibyshev reservoir for 2009-2015 yrs is shown in fig. 1.

The highest multiyear average monthly concentration of ammonium ions was observed in February during the winter low-water period and may be due both to the discharge of insufficiently treated wastewater into the Kuibyshev reservoir and its tributaries, and the lack of vegetation of aquatic vegetation. Starting with the rise and peak phases of the flood, the average concentrations of ammonium ions decrease and reach their minimum value in June in the summer low-water phase, which may be due to their consumption by aquatic vegetation. In August and September, there is a slight increase to 0.79 and 0.80 MPC respectively, caused by a decrease in the consumption of ammonium ions by aquatic vegetation and their transformation into nitrite - and nitrate - ions.
Nitrate ions. Seasonal variability of perennial average monthly concentrations of nitrate ions in the water of the Kuibyshev reservoir for 2009-2015 yrs is shown in fig. 2.

Analysis of fig. 2 allowed us to identify certain patterns in the fluctuations of the concentration of nitrate ions by seasons of the year. From mid-February to mid-April (by the end of the winter drawdown of the reservoir), an increase in the concentration of nitrate ions is observed. Such periods of increasing concentrations of nitrate ions are attributed by researchers to the predominance of the decomposition of organic matter and the mineralization of nitrogen (nitrification process) with its minimum consumption by higher aquatic vegetation and phytoplankton, as well as to the entry of nitrate ions in the composition of the groundwater of rivers.

The formation of nitrate ions as a result of nitrification in the reservoir during this period is difficult, since during the freezing-up period there is a characteristic deterioration in the oxygen regime [13].

Further, until mid-August in the water of the Kuibyshev reservoir, a decrease in the concentration of nitrate ions is observed as a result of the self-purification process caused by the active absorption of nitrate ions by lower and higher aquatic vegetation. A similar seasonal pattern of concentrations of nitrate ions was noted in the works of M. Kumani for small and medium-sized rivers of the Central Black Earth Region [14, 15]. After the summer minimum, the concentration begins to increase again, which is caused by the decomposition of aquatic vegetation.

Nitrite ions are an intermediate product of redox processes and, as a result, are usually found in the water column of natural waters in small quantities. The presence of nitrite in water in significant amounts indicates the intensity of oxidative processes as a result of the active activity of microorganisms and can be used as an indirect criterion of pollution. The increased content of nitrite ions indicates an increase in the decomposition of organic substances under conditions of a slower oxidation of nitrite ions to nitrate ions [16]. In addition, in the summer there are frequent cases of lack of oxygen consumed for the oxidation of organic matter. In such cases, under anaerobic conditions, nitrates are reduced by microorganisms - denitrifiers, using nitrate-ion as the final electron acceptor during the oxidation of various organic substrates and molecular hydrogen.

Seasonal variability of perennial average monthly concentrations of nitrite ions in the water of the Kuibyshev reservoir for 2009-2015 yrs is shown in fig. 3.
Figure 3. Seasonal variability of long-term average monthly concentrations of nitrite ions in the water of the Kuibyshev reservoir for 2009-2015 yrs.

Phosphate ions. Seasonal variability of perennial average monthly concentrations of phosphate ions in the water of the Kuibyshev reservoir for 2009-2015 yrs is shown in fig. 4. During the study period, we discovered some features of the course of mean multiyear monthly concentrations of phosphate ions. Seasonal variability of multiyear average monthly concentrations in the Kuibyshev reservoir is characterized by the presence of two maxima (in March and November) and one minimum in May (the minimum concentration is 0.29 MPC). The perennial average monthly concentration of phosphate ions for the period from 2009 to 2015 yrs amounted to 0.48 MPC. Such fluctuations in the concentrations of phosphate ions are due to seasonal changes in the number of phytoplankton and higher aquatic vegetation, the dynamics of natural waters and anthropogenic effects.

The formation of the first maximum of phosphate ion concentrations by the end of the freezing winter period in March (the maximum concentration is 0.59 MPC) may be due to diffuse phosphate discharge from the urbanized territory of the Kuybyshev reservoir and its tributaries on the flood rise with an insignificant amount of vegetation consuming this element in the freeze-up period.

The second maximum was detected in November (0.58 MPC) before freezing, which may be due to a drop in temperature, accompanied by the regeneration of phosphates when phytoplankton dies out against the background of the absence of phosphate consumption - ions of higher and lower aquatic vegetation.

A significant decrease in phosphate ions at the peak of the high water in May (the minimum concentration is 0.29 MPC), associated with the active development of bacteria, algae and cyanobacteria, for which these substances are a nutrient medium. In addition, during this period there is an intensive dilution due to the filling of the Kuibyshev reservoir and the water releases through the dam during the flood period.

A similar seasonal dynamics of phosphate ions has been noted in a number of works both on the Kuibyshev reservoir for an earlier period of years [17], as well as on other water bodies [18]. It is noted that during intensive phytoplankton bloom the amount of phosphate ions in some water bodies may drop to an analytical zero, and in the pre-vegetation period it reaches a maximum [19].

In general, the analysis of the results of observations for 2009-2015 yrs showed that in the water of the Kuibyshev reservoir seasonal variability is characteristic of all nutrients, it is most pronounced in nitrate ions (Fig. 2). During the season, the long-term average monthly concentration of nitrate ions changed 7.2 times, which is in good agreement with the results given in [20] for the Saratov reservoir.
4. Conclusions
The results of the study show that in 2009-2015 yrs perennial average monthly concentrations of biogenic substances (ammonium ions, nitrate ions, nitrite ions, phosphate ions) did not exceed the fisheries standards in the water of the Kuibyshev reservoir.

It is established that in the period 2009-2015 yrs from February to November, there was a noticeable tendency of a decrease in multiyear average monthly concentrations of ammonium ions and a moderate tendency of a decrease in multiyear average monthly concentrations of nitrate ions.

It is shown that in the period 2009-2015 yrs the seasonal variability of multiyear average monthly concentrations of nitrate ions in the Kuibyshev reservoir was characterized by the presence of one maximum in the month of May and two minima in February and November. The seasonal variability of long-term averages of monthly concentrations of phosphate ions in the Kuibyshev reservoir was characterized by the presence of two maxima (in March and November) and one maximum in May.

It was revealed that all the biogenic substances in the water of the Kuibyshev reservoir are characterized by seasonal variability, which is most pronounced in nitrate ions.

In order to improve the water quality of the Kuibyshev reservoir, it is necessary to reduce the nutrient load by reducing the diffuse discharge by planting and tinning water protection zones, cleaning wastewater and melt water of settlements and large industrial complexes located in the catchment area of the Kuibyshev reservoir and its tributaries. In addition, it is necessary to continue work on further improvement of the purification from biogenic substances (especially from phosphate ions) of wastewater from industrial and municipal enterprises that discharge into the Kuibyshev reservoir and its tributaries.

The obtained results can be used in the preparation of republican, municipal and industrial programs to reduce the nutrient load on the waters of the Kuibyshev reservoir and its tributaries and to optimize the monitoring system for nutrients.

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