Problems of epy limiting the processes of epy eutrophication in a slightly saline reservoir

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Abstract. One of the most difficult for solving environmental problems of water bodies around the world is the ever-accelerating processes of eutrophication, which are currently mostly anthropogenic in nature. The aim of the work is to identify the biogenic matter that has the greatest influence on the processes of eutrophication and, consequently, limits this process. To clarify this agent of eutrophication, a model experiment was carried out, consisting of a series of tests with the natural water sampled from the Gulf of Taganrog of the Sea of Azov. When solving the problem of the need for and the degree of removal of the biogens from the wastewater, first, the attention should be paid to the biogen that limits the eutrophication of this water system.

1. Introduction
One of the most difficult for solving environmental problems of water bodies around the world is the ever-accelerating processes of eutrophication, which are currently mostly anthropogenic in nature. In this regard, the problems of limiting the eutrophication processes are relevant. It is necessary to look for the ways to reduce the anthropogenic biogenic load in the water area. It is known that the processes of eutrophication of waters occur with the participation of mainly two biogenic components of ecosystems, namely, nitrogen and phosphorus. Accordingly, the aim of the work is to identify the biogenic matter that has the greatest influence on the processes of eutrophication and, as a consequence, limits this process. To clarify this agent of eutrophication, a model experiment was carried out, consisting of a series of tests with the natural water sampled from the Gulf of Taganrog of the Sea of Azov. Moreover, when solving the problem of the need for and the degree of removal of the biogens from the wastewater, first of all, the attention should be paid to the biogen that limits the eutrophication of this water system.

2. Materials and methods
When solving the problem of the limiting productivity, i.e. limiting the processes of eutrophication, it is necessary to determine what it depends on. In general, this phenomenon is limited by three main abiotic factors, namely, water temperature, solar radiation penetrating into the water column, and biogenic elements [1]. The first factor entirely depends on the zonal geographical patterns (if we do not take into account the global climate change on the Earth) and refers to completely unregulated external influences on the ecosystem. Solar radiation also depends on the geographic zoning, but
unlike the water temperature, in rare cases (with hyper eutrophication of a water body and strong turbidity) it can affect the processes of eutrophication. However, the waters of the Gulf of Taganrog of the Sea of Azov are not hyper eutrophic ones. Thus, in the problem of limiting the processes of eutrophication, the biogenic substances come to the fore. Therefore, when studying this phenomenon, it is important to establish which of the biogenic elements limits the primary production processes. It is important to note that anthropogenic sources play an important role in the supply of the biogens to the water body, contributing to the development of eutrophication and accelerated changes in the ecosystem of a water body.

Studies based on the generalization of data from monitoring the eutrophication of water bodies confirm the leading role of nitrogen and phosphorus in the processes of increasing the eutrophic index [1].

Thus, the limitation in the model experiment can be determined by adding the biogenic additives to the water sample, i.e. compounds of nitrogen and phosphorus.

Three series of experiments were carried out. The initial samples were taken in the Gulf of Taganrog of the Azov Sea. Each series of the model experiment includes a daily measurement of these indicators during five days.

Each water sample was placed in a transparent vessel with a volume of 1000 ml. Thus, the sample contained an optimally thin layer of water, which provided sufficient air exchange, and therefore these conditions can be equated to natural ones.

During all series of the experiment, one sample always remained the control one, i.e. remained without any biogenic additives. The remaining 6 samples were supplemented with compounds of phosphorus (KH2PO4) and nitrogen (NH4Cl).

Seven samples were measured daily for seven indicators. Thus, one series of samples includes 245 measurements; the total number of measurements is 735.

Such concentrations of nitrogen and phosphorus, which would approximately correspond to the atomic-weight ratio of these elements in water bodies, were chosen. The phosphate concentrations were: 1.36 mg/dm3 (sample 1), 1.09 mg/dm3 (sample 2), 0.41 mg/dm3 (sample 3), and the nitrogen ones, respectively: 2.67 mg/dm3 (sample 4), 1.91 mg/dm3 (sample 5), 1.146 mg/dm3 (sample 6). The selected concentrations corresponded approximately to the atomic-weight ratio of the nitrogen and phosphorus in the water of the Gulf of Taganrog during the study period.

Further, for a comparative assessment of the effect of the nitrogen and phosphorus on the rate of the eutrophication processes, the change in the indicator in the experiments relative to control were calculated (the effect of the influence of the biogenic additives) [2]:

\[
A_{\text{biogen}} = \left( \frac{\Delta T_{\text{sample}} - \Delta T_{\text{control}}}{\Delta T_{\text{control}}} \right) \times 100\%,
\]

where \(A_{\text{biogen}}\) – the effect of the influence of the biogenic additives, %; 
\(\Delta T_{\text{sample}}\) and \(\Delta T_{\text{control}}\) – the change in the value of the eutrophic index in the experiment and the control sample, respectively.

To solve the problem of the need for and the degree of the removal of the biogenic matter from the wastewater, first, the attention should be paid to the biogen that limits the eutrophication of a given water system [2]. To clarify this element, a series of experiments were carried out with natural water from the Gulf of Taganrog.

The concentration of the nitrate, ammonium ion, phosphate, as well as the water temperature, salinity, and pH were determined as the indicators of the water eutrophication. These components correspond to the components of the previously obtained regression model of the eutrophication of the northeastern part of the Gulf of Taganrog of Sea of Azov [3]:

\[
T = 6.294 + 0.104(S) + 0.114(\tau) - 1.06(NH_4) + 0.021(NO_3) - 0.929(PO_4),
\]

where \(T\) – waters eutrophic index; 
\(S\) – salinity, %;
t – water temperature, °C;
NH₄ – ammonium concentration, mg/dm³;
NO₃ – nitrate concentration, mg/dm³;
PO₄ – phosphate concentration, mg/dm³.

3. Results
Examples of the data obtained are shown in Table 1.

| Indicator/Time | % | t | NH₄ | NO₃ | PO₄ | NO₂ | pH | T |
|---------------|---|---|-----|-----|-----|-----|----|---|
| 1 day         | 1.9 | 22.0 | 0.157 | 0.269 | 0.211 | 0.031 | 8.71 | 8.64 |
| 2 day         | 1.8 | 22.0 | 0.145 | 0.207 | 0.206 | 0.023 | 8.61 | 8.65 |
| 3 day         | 1.7 | 22.0 | 0.138 | 0.184 | 0.190 | 0.006 | 8.68 | 8.66 |
| 4 day         | 1.7 | 22.0 | 0.130 | 0.139 | 0.164 | 0.007 | 8.71 | 8.69 |
| 5 day         | 1.9 | 22.0 | 0.126 | 0.152 | 0.141 | 0.011 | 8.69 | 8.74 |

When determining the effect of the influence of the biogenic additives on the eutrophic index of the waters of the Gulf of Taganrog, an analysis of the correlation dependence was carried out between samples with the addition of a phosphorus-containing compound and samples with the addition of a nitrogen-containing compound. The absence of a correlation shows that the effect of the influence of the biogenic nitrogen and phosphorus supplements is not summarized. The presented research results showed [3]:

- the lack of correlation between the ammonium ion and phosphate concentrations in all studied samples;
- the high dependence of the eutrophic index on the concentration of ammonium ion;
- a rather low correlation dependence of the eutrophic index on the phosphate concentration.

The effect of the influence of biogenic additives on the rate of eutrophication of waters in the northeastern part of the Taganrog Bay, calculated according to formula 1, is presented in Table 2. Consequently, it can be seen that the effect of nitrogen is almost three times higher than the effect of phosphorus.

| KH₂PO₄ | NH₄Cl |
|--------|-------|
| [P], mg/dm³ | A, % | [N], mg/dm³ | A, % |
| 1.36 | 22.47 | 2.67 | 51.55 |
| 1.09 | 16.49 | 1.91 | 45.65 |
| 0.41 | 10.14 | 1.146 | 38.17 |
| The average value | 16.37 | The average value | 45.12 |

4. Conclusions
Based on the studies, it can be concluded that the leading role of nitrogen in the processes of the eutrophication is currently characteristic of the Gulf of Taganrog of the Sea of Azov.

Waters eutrophication becomes most probable when the atomic weight ratio of nitrogen and phosphorus (N:P) approaches the atomic weight ratio of these elements in phytoplankton, i.e. 16:1.
It should be noticed that the long-term changes in the concentrations of nitrogen and phosphorus in the Gulf of Taganrog are described by the scientists [4-9]. The comparative analysis of long-term fluctuations of the biogenic matter in the waters of the Sea of Azov, according to the authors, showed the presence of different ratios of the concentrations of nitrogen and phosphorus compounds. So, periods with the increased concentrations of nitrogen, as a rule, are distinguished by the high water content, reduced wind activity and the increased temperature background. Fluctuations in phosphorus concentrations depend on the influx of the fresh water to the Gulf. The phosphorus concentration decreases comparatively sharply in dry years and increases just as significantly in high-water years. Unlike nitrogen compounds, wind activity over the water area and an increased temperature background have a direct effect on the increase in the amount of total phosphorus concentrations in the water.

According to Makarov [10], who studied the concentrations of nitrogen and phosphorus in the Sea of Azov in 1985–1995, the increase in the concentration of mineral phosphorus was fixed, especially in the Gulf of Taganrog.

According to Alexandrova [5], who analyzed the regime of biogenic substances in 1988-2000, the intensive assimilation of the nitrate concentrations by phytoplankton lead to the biogens decrease in the sea for 1996-2000. In the Gulf of Taganrog this phenomenon is due to the biological factors and the weakening of the anthropogenic impact, while in the years characterized by the development of production and the large-scale use of the agrochemicals (1985-1990), the amount of nitrate concentrations was several times higher. The trend towards the decrease in the concentration of phosphate appeared later (since 1997), when the concentrations decreased by 1.3 times compared to the first half of the 90s. At the same time, the inflow of the biogenic matter with the river runoff, despite some growth, remained at the same level, which is apparently associated with the decrease in the concentration in the river waters due to the decrease in the impact of the anthropogenic factors.

According to the Matishov's data [6], the lesser consistency between long-term fluctuations in the biogens, river runoff and salinity of the Sea of Azov is explained by the events that occurred at the end of the 20th century: the sharp changes in climate-forming processes in the atmosphere in general, wind and thermal fields in particular, as well as the degree of their influence on the elements of the water balance and oceanographic parameters.

According to Studenikina [8,9], who studied the content of the biogens in the Sea of Azov in 1958-1998, the concentration of the mineral nitrogen increased twice in 1958-1987, and then decreased 1.9 times in 1988-1998. The concentration of the mineral phosphorus in the specified period has doubled. The ratio of nitrogen to phosphorus is typically 2-3 times lower.

Thus, the conducted literature analysis showed the heterogeneity of changes in the long-term concentrations of the nitrogen and phosphorus in the Gulf of Taganrog, which allows us to speak of the variable significance of their influence on the processes of the eutrophication.

The article authors analysis (2002-2015) [3, 11, 12, 13], the constructed statistical model, the experimental studies allow to conclude that nitrogen is currently the limiting factor in the eutrophication of the Gulf Taganrog.

That is to say that according to all the data we have obtained, the ecological situation that has formed for the Gulf of Taganrog of the Sea of Azov is that the nitrogenous compounds limit the eutrophication of the water area.

Consequently, the analysis of the literature, the authors research on determining the eutrophic index of the waters, the ecologically permissible concentrations of the ammonium ion, nitrate and phosphate, their ecological reserves, the total external load on the gulf and the biogen limiting the eutrophication processes, allow us to formulate the main measures to reduce the concentration of nutrients in the water area of the Gulf of Taganrog, and as a consequence of slowing down the processes of its eutrophication:
• the increase of the additional purification of the wastewater from nitrogen- and phosphorus-containing compounds;
• the planned control of the practical needs in the use of arable land in a legislative way, rational use of land and, as a result, ensuring the minimum transfer of the biogens from the land to the water area of the Gulf of Taganrog;
• the reduction of nitrogen load on the waters of the gulf. However, this path, as a rule, is difficult to implement: the sources of nitrogen compounds are not localized, numerous, heterogeneous and are associated with such aspects of human activity, the limitation of which requires a change in the lifestyle of millions of people;
• the chemical methods of the precipitation of the compounds and physicochemical methods of "fight" against the blue-green algae: the mechanical removal of the biomass, aeration of the vast territories, the use of the algicide preparations and coagulant substances, the use of the ultrasound. Not all these methods are cheap and ineffective, and the introduction of the algicide compounds adversely affects the life of the other aquatic organisms.

Accordingly, in order to overcome the undesirable consequences of the eutrophication of the waters of the Gulf of Taganrog of the Azov Sea, it is necessary to develop and implement a set of the environmental measures and methods for managing the ecological systems.

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