Approaches to Management of Anthropogenic Eutrophication Caused by Loading from Mineral Fertilizers

E A Minakova¹, A P Shlichkov², A V Arinina³

¹Kazan Federal University, Institute of Fundamental Medicine and Biology, Kazan 420008, Kremlyovskaya street 18, Russia
²Institute of Ecology and Mineral Sciences of the Republic of Tatarstan, Kazan 420087, Daurskaya street 28, Russia

E-mail: ekologyhel@mail.ru

Abstract. The main driving force for eutrophication of water bodies are biogenic elements (compounds of nitrogen, phosphorus, carbon). These elements are the most important components of natural waters, which determine biological productivity. In this work, an approach based on taking into account hydrometeorological values is developed with the aim of limiting the entry of nutrient elements into the surface with runoff from agrarian lands (for example, the Kazanka River). The results of a joint analysis of the temperature and atmospheric precipitation regime, the dynamics of nitrogen and phosphorus fertilizer application, and the concentrations of nutrients in the water of the river Kazanka are given. Regression equations describing the dependence of the concentrations of nutrient substances on the investigated factors are obtained.

1. Introduction
The process of anthropogenic eutrophication is a consequence of the disturbance of the sustainability of aquatic ecosystems and, in the degree of the danger of global anthropogenic impact on the environment, was put in the first place at the XXII Session of UNEP in 1984 [1].

The main driving force for eutrophication of water bodies are biogenic elements (compounds of nitrogen, phosphorus, carbon). These elements are the most important components of natural waters, which determine biological productivity. The excessive amount of nutrients triggers the intensive growth of aquatic vegetation, which ultimately affects the quality of water. The main anthropogenic sources that pollute water bodies with nutrients are organized sources (discharges of industrial and communal enterprises), as well as unorganized (diffuse) sources (livestock farms, agricultural lands, surface runoff from urban areas).

To date, to preserve the ecological safety of water bodies and watercourses, the key task is to find ways to manage the processes of eutrophication, which is a key task for preserving the ecological safety of water bodies and streams. At the same time, the leading role is given to the ecological regulation of the permissible anthropogenic load of organic matter, taking into account the ability of the aquatic ecosystem to be stable, as its most important property.

More than two decades ago, Russia posed the question of the need to determine the permissible environmental loads and adequate restrictions (rationing) of existing anthropogenic impacts, taking into account the totality of possible harmful effects of many factors and the natural specifics of the
facilities. According to [2], an allowable load is considered to be "under the influence of which the deviation from the normal state of the system does not exceed natural changes and, therefore, does not cause undesirable consequences in living organisms and does not lead to a deterioration in the quality of the environment."

In general, environmental rationing is not a substitute for sanitary and hygienic rationing, but, in a sense, supplements it, tightening the applied standards [3]. Environmental rationing is a key problem in the formation of environmental safety. Clarification of the regional ecologically permissible levels of nutrients impact on the ecosystem is certainly necessary.

In the modern period, the biogeochemical cycles of phosphorus and nitrogen, the main components of the formation of the processes of eutrophication, are subject to significant anthropogenic transformations. The use of mineral fertilizers is an essential factor of anthropogenic interference in the cycle of biogenic elements. According to modern ideas on the flow of fertilizers from the territory [4, 5], the largest part of nitrogen (34-60%) and a significant part of phosphorus (9-25%) fertilizers enter the reservoirs from agricultural lands, and the amount of runoff is determined by the reserve of biogenic elements in the soil and physic geographic location of the regions.

Of particular relevance is the assessment of the influence of climatic factors of moisture and heat transfer on the surface run-off of biogenic elements from agricultural lands in a changing climate. Primary production of terrestrial ecosystems is controlled by environmental factors - temperature, precipitation and evaporation [6, 7, 8, 9]. Assessing the impact of the components of moisture and heat transfer in the face of climate change is very important at both the global and regional levels. In works [10, 11], the opinion is expressed that the climate can significantly influence the decrease or increase in the flow of cations from the catchment area. On the other hand, processes in the catchment area with warming accelerate the growth of plants and the absorption of nutrients, the processes of oxidation and reduction. In addition, according to [12], in the warm climate, the production processes in the reservoir and in the catchment area increase, which ultimately leads to eutrophication of the waters. The peculiarity of the period chosen for the study is the considerable variability of the air temperature and precipitation indicators in comparison with the norm.

Of particular relevance is the assessment of the influence of climatic factors of moisture and heat transfer on the surface run-off of biogenic elements from agricultural lands in a changing climate. In addition to the existing methods for estimating the permissible biogenic load on agricultural landscapes, an approach based on taking into account meteorological values is developed in order to limit the entry of biogenic elements into the water of rivers with surface runoff from agrarian lands (for example, the Kazanka River).

In the formulation of studies of such multifactorial phenomena, it is advisable to limit them to specific representative space-time coverage at the regional level.

Investigation of the phenomena caused by the influence of many factors, it is advisable to conduct for specific water bodies or watercourses. As the object of investigation in this paper, the Kazanka river with feeding its tributaries. The river experiences mainly agrotechnogenic loads: most of the catchment area is occupied by arable land - 72%, forests occupy 13%, meadows - 5%. The analysis of state statistical reporting on the use of water carried out by the authors shows that in the Kazanka receives discharges of about eighty objects of the economy. In addition, 49 agricultural facilities are located on the watershed of the river. Previous studies [5] found that the contribution of organized sources of pollution to the formation of quality of river water in the background and closing areas does not exceed 7%.

The main purpose of this work is to assess the permissible biogenic load on the agrolandscape, based on taking into account meteorological factors in order to limit the entry of nutrients into the water of rivers with runoff from agrarian lands (for example, the Kazanka river basin).

2. Materials and Methods
The work used materials of meteorological observations and data of the Department for Hydrometeorology and Environmental Monitoring of the Republic of Tatarstan (RT) of the Kazanka
river for the flow (for the period 1991-1996) and for the pollution with nitrogen and phosphorus compounds in the background and closing lines for the period 1987-1995, data on the amount of deposition and the chemical composition of atmospheric precipitation, at meteorological stations of the RT region; State statistical reporting data enterprises located on the catchment area; materials of the Ministry of Agriculture and Food of the RT on the introduction of mineral fertilizers for agricultural crops, as well as own experimental materials relating to individual years and obtained using standard methods recommended for use in the Russian Hydrometeorological Network.

For definition of quantitative communications between values of studied sizes used a method of multiple linear correlations. The importance of the received coefficients of correlation (r) estimated by means of t-criterion Student with use of transformation of Fischer for r. For a studied data file (n ≥ 9) the correlation dependences characterized by size r ≥ 0,75, are significant with probability P> 0,95.

In work the analysis is executed:
- Natural factors of external influence on the quality of river water - meteorological and hydrological values: (mean annual values of water flow, air temperature (T), the amount of atmospheric precipitation (R) across the river basin and data on the composition of atmospheric deposition);
- parameters of anthropogenic load on the catchment area - the mass of mineral phosphorus (S_P) - and nitrogen containing (S_N) fertilizers added annually;
- characteristics of biogenic elements in the water of the (discharges and surface runoff; mean annual and average for the period of observation of the concentration of biogenic elements of phosphorus and nitrogen and the multiplicity of exceeding of the fishery standards of maximum permissible concentrations).

3. Results and Discussion
Dynamics and trend of the mass of nitrogen (S_N) and phosphorus (S_P) fertilizers introduced in the catchment area of the Kazanka river basin is shown in Fig. 1. On the basis of the database on nitrogen and phosphorus fertilizers applied to the watershed of the can be traced the variability of these indicators in retrospect of years.

![SN, Sp, centners per hectare](Image)

Figure 1. Dynamics and trend of nitrogen and phosphorus fertilizers application in the Kazanka river basin.
The analysis of Fig. 2 shows that for the period from 1987 to 1995 years, there is a moderate tendency to increase the application of nitrogen fertilizers ($S_N$). In general, over the period, the increase in $S_N$ was 0.24 centners per hectare. At the same time there is a weak tendency to reduce the application of phosphorus fertilizers ($S_p$). In general, during the period, the decrease in $S_p$ was 0.48 centners per hectare.

**Air temperature** The location of the territory of the RT in the depth of the continent of temperate latitudes determines the development of atmospheric processes in the direction of strengthening the continental weather and climate. On the territory of the republic there is an intensive transformation of air masses, which is accompanied by a cooling in winter, and in summer - heating. The average annual air temperature varies in the territory of the RT in the range from 2.0 to 3.1 [13]. The temperature regime plays an important role in the physical and biological processes of eutrophication of water bodies [14].

**Precipitation** from 1989 to 1994 years the tendency of decrease in average annual temperatures of air on catchment of the river was observed in Kazanka river basin, the total decrease over this period was about 1.8 C°. From 1994 to 1995 years there is an increase in the average annual air temperature in the catchment area in the Kazanka river basin is 3.1 C°.

**Nutrients: Phosphorus** among a variety of nutrient elements plays a decisive limiting role in the processes of eutrophication for the water bodies of the temperate zone. The cycle of phosphorus in the environment is not closed and has a sedimentary orientation. The main natural source of phosphorus is the erosion of mountain and sedimentary rocks, clayey materials and peatlands. Anthropogenic sources of phosphorus are waste water and fertilizer and farm livestock wastes run-off from the catchment area. The main factor determining the concentration of phosphorus in natural water bodies is the exchange between its inorganic forms on the one hand, and living organisms on the other. Compared with nitrogen phosphorus is more mobile and the rate of turnover of phosphorus is much higher. This exchange is carried out with two oppositely directed processes - photosynthesis and decomposition of organic matter. With its additional input in the sewage composition, this ratio changes and phosphorus accumulates in water bodies with a complex of subsequent disturbances in the ecosystem [15].

We obtained the multiple regression equations that describe the variability of phosphate ion concentrations in the river water, depending on the meteorological values and dosage of phosphorus fertilizers. Thus, the variability of phosphate ion concentrations in river water is described by the multiple regression equation:

$$C_p = 1.15S_p + 0.08T - 0.97$$  \(1\)

where $C_p$ (total) - the phosphate ion concentration in the river water, mg/L; $S_p$ - the mass of phosphorus fertilizers introduced, centners per hectare; $T$ - the average annual temperature of atmospheric air in the catchment area in the Kazanka river basin, C°.

In the regression equation (1), the coefficient of multiple correlation between the value of $C_p$ (total) and the factors $S_p$ and $T$ is 0.95. The correlation coefficient is significant at the level $\alpha = 0.05$. The factors $S_p$ and $T$ determine 91% of the variance $C_p$ (total). For the analyzed case $R^2 = 0.9$, which indicates a very high connection between the value of $C_p$ (total) and the factors $S_p$ and $T$.

**Nutrients: nitrogen**, unlike phosphorus, is a water and air migrant because of its high solubility of its mineral and volatility of gaseous compounds. Along with phosphorus, nitrogen initiates the launch of eutrophication processes in waterways and reservoirs, which leads to an increase in production processes with the accumulation of organic matter.

The average weighted annual concentration of ammonium ions in atmospheric precipitation practically does not change, while the concentration of nitrite ions in atmospheric precipitation increases significantly, with the total content increasing with time, exceeding the corresponding concentration of sulfate ions in recent years. In general, during the period under study, the density of precipitation of nitrates with atmospheric precipitation in the RT region was 1.08-3.24, and that of
ammonium cation \(0.37-0.96 \text{ g} / (\text{m}^2 / \text{year})\) [18], which significantly exceeds the annual load these ions in the regions of Russia.

Earlier we showed that ammonium ion is a priority pollutant in the Kazanka river basin [19], which was decisive when choosing the studied form of nitrogen. In addition, studies on the distribution of nitrogen-containing compounds in the European part of Russia [20] have shown that nitrate forms predominate in regions with developed industry, and ammonium form in regions with developed agriculture.

This circumstance allows us to make the assumption that in the basin of the Kazanka river is the main contributor to the nutrient load of nitrogen compounds by agriculture. A close relationship has been established between the concentration of the ammonium ion (\(C_N (NH_4)\)) in the water of the river. Kazanka depending on meteorological values and anthropogenic factors. The variability of ammonium ion concentrations in the river water, depending on the meteorological values and doses of phosphorus fertilizers, is described by the multiple regression equation:

\[
C_N (NH_4) = 0.992S_N + 0.003R - 0.71
\]

where \(C_N (NH_4)\) - concentration of ammonium-ion in the river water, mg/L; \(S_N\) value of nitrogen fertilizers introduced in the Kazanka river basin, centners per hectare; \(R\) - value of the average monthly precipitation for April in the Kazanka river basin according to meteorological stations, mm.

In the regression equation (2), the coefficient of multiple correlation between the value of \(C_N (NH_4)\) and the factors \(S_N\) and \(R\) is 0.96. The correlation coefficient is significant at the level \(\alpha = 0.05\). The factors \(S_N\) and \(R\) determine 93% of the \(S_N\) variance. For the analyzed case \(R^2> 0.9\), which indicates a very high connection between the value of Samson and the factors \(S_N\) and \(R\).

The obtained dependences allowed to calculate the rate of fertilizer application depending on the variability of meteorological quantities. At the projected maximum values of the average annual air temperature in the Kazanka river basin is capable of applying phosphate fertilizers up to 60, and at minimal - up to 81 kg per hectare. To ensure water quality standards in the Kazanka river basin in ammonium-ion in the river water, with projected maximum precipitation values in April, it is possible to apply nitrogen fertilizers to 139 kg per hectare, and minimum ones to 124 kg per hectare.

4. Conclusions
An approach is proposed for calculating the maximum permissible rate of application of mineral fertilizers, taking into account the meteorological characteristics of the catchment area, aimed at achieving the standards for the water quality of the Kazanka river. The use of this approach will allow to adjust the dosage values of phosphorus and nitrogen fertilizers taking into account the forecast values of meteorological values that will not only promote the rational use of expensive mineral fertilizers but also minimize the pollution of river waters and create optimal conditions for sustainable water use.

The dependence of the concentration of phosphate and ammonium ions in water was established Kazanka from meteorological values (air temperature, the sum of atmospheric precipitation) and doses of fertilizer application in the catchment area. This regularity is connected with the peculiarities of geochemical cycles of biogenic elements.

The proposed approach can be used to calculate regional standards for the doses of phosphorus and nitrogen fertilizers at river watersheds in the European territory of the Russian Federation, which will not only improve crop yields and rational use of expensive mineral fertilizers, but also minimize pollution of river waters and create optimal conditions for the use of water resources by economic entities.

5. References
[1] Hirsanov N I and Osipov G K 1993 Control of eutrophication of reservoirs (Leningrad: Gidrometeoizdat) p 278
[2] Izrael Yu A 1984 *Ecology and control of the state of the natural environment* (Moscow: Gidrometeoizdat) p 560
[3] Pavlov D S, Rosenberg G S and Shatunovsky M I 2011 *Issues of ecological rationing and development of a system for assessing the state of water bodies* (Moscow: Association of Scientific Publications) p 196
[4] Coplan-Dix and EA Stravinskaya 1993 *Anthropogenic redistribution of organic matter in the biosphere* (St. Petersburg: Science) p 206
[5] Latypova V Z, Selivanovskaya S Yu, Stepanova N Yu and Minakova E A 2005 *Scien. notes of Kazan State Univ.* 147 159-170
[6] Isachenko A G 1953 *Basic issues of physical geography* (Leningrad: Publishing House of Leningrad State University) p 391
[7] Lit H 1974 *Ecology* 13-23
[8] Rosenzweig M L 1968 *Amer. Nat* 102 pp 67-74
[9] Schuur A G 2003 *Ecology* 84 1165-1170
[10] Sereda J 2011 *Limnologica* 41 1-9
[11] Wright R F and Dillon P J 2008 *Hydrol. Earth System Sci.* 12 333-335
[12] Feuchtmayr H. 2009 *J. Appl. Ecol* 46 713-723
[13] Kolobov N V 1983 *The climate of the Tatarstan* (Kazan Publishing House University) p 160
[14] Henderson-Sellers B and Markland H R 1990 *Dying Lakes: Causes and Control of Anthropogenic Eradication* (Leningrad: Gidrometeoizdat) p 278
[15] Rossolimo L L 1977 *Changes in liminal ecosystems under the influence of anthropogenic factor* (M: Nauka) - p 205.
[16] Baranov E E and Seleznev V A 2013 *Probl. of Reg. and Glob. Ecol.* 23 160 - 166
[17] Minakova E A, Latypova V Z, Yakovleva O G and Semanov D A 2001 *Ecol chemistry* 10 115 – 120
[18] Latypova V Z, Yakovleva O G, Minakova E A, Zhdanova G N and Zakharov S D 2006 *Kazan: Kazan St. Univ. Press* 148 24 - 29
[19] Minakova E A. 2004 *Accounting for meteorological factors in surface water quality management (on the example of the rivers Kazanka, Sviyaga, Stepnoi Zai)* (St. Petersburg) p 147
[20] Moiseenko T I and Rudneva I I 2008 *Rep. of the Academy of Sci.* 420 395-400