Quantitative assessment of biogenic elements and suspended matter load to inner-city river: the role of point sources and diffuse runoff

R N Sabanaev, O V Nikitin, V Z Latypova, E A Minakova and N Yu Stepanova

1 Kazan Federal University, 18 Kremlyovskaya St., Kazan, 420008, Russia
2 Institute for Problems of Ecology and Mineral Wealth Use of Tatarstan Academy of Sciences, 28 Daurskaya St., Kazan, 420087, Russia

3E-mail oleg.nikitin@kpfu.ru

Abstract. The article provides a quantitative assessment of the input of biogenic elements and suspended matter in the composition of the storm sewer outlets from the territory of the Kazan City (Russia, the Republic of Tatarstan) and the diffuse runoff of biogenic elements from the agro-developed catchments into the Kazanka River (left tributary of the Volga River) as the main risk factors for the development of anthropogenic eutrophication processes. Based on the results of long-term monitoring and the current background concentrations of total phosphorus, nitrogen and suspended solids in the recipient river, determined in the work, the impact of storm water discharge on surface waters within the Kazan City was assessed. The values of permissible loads of phosphorus and nitrogen mineral fertilizers on an agriculturally developed catchment are given for regulating the diffuse runoff of nutrients into a water body, depending on the hydrometeorological conditions of the territory, to a level that meets the basic environmental requirements for the quality of surface waters.

1. Introduction

Analysis of the ecological state of the vast Volga basin reveals the main generally similar problems associated mainly with the course of practically uncontrolled processes that really threaten the state of the Volga. These include, first of all, storm sewer outlets of large cities of Russia, carrying mud flows practically without purification into surface waters; An even larger process is diffuse runoff coming from agrarian and industrially developed catchments, settlements, objects of accumulated environmental damage (landfills, cattle burial grounds, etc.), with the discharge of groundwater, with river runoff, etc. Both of these processes allow the mechanism of anthropogenic eutrophication in the waters of the Volga basin and the associated so-called “blooming” of water due to the intake of an excess amount of nutrients, as well as siltation and shallowing of rivers due to the intake of suspended matter. The fact that the state of the Volga is not improving, despite the measures taken in previous years, is generally associated with a weak demand for scientific and technological advances in the study of the main regularities of these processes, quantitative assessment of their contribution to the formation of surface water quality and substantiation of adequate priorities in planning water management activities in the catchment [1], [2].
The aim of this work is a quantitative assessment of the input of nutrients, suspended matter in the composition of the storm sewer outlets from the city territory and the diffuse runoff of nutrients from the agro-developed catchments into the intra-city water body.

2. Materials and methods
The object of the study was the Kazanka River (left tributary of the Volga River), which receives pollutants in the mouth part as part of storm wastewater outlets from the territory of the Kazan City (55°48'27.1" N, 49°06'34.2" E) and diffuse runoff from the upstream catchment (2600 km²), most of which is occupied by arable land (72%), forests occupy 13%, meadows - 5% of the territory; the contribution of wastewater discharges from industrial enterprises to the formation of river water quality in the background and outlet sections does not exceed 7% [3].

Monitoring of storm sewage discharges from the territory of the Kazan City and surface waters of the Kazanka River was carried out during expedition trips, seasonal sampling and field surveys during 2014–2017; as well as during monthly water sampling during 2014 and 2016 in background stations for special experiments to determine the background concentrations of pollutants in surface waters according to methodological recommendations [4]. The selection and chemical-analytical studies of water samples were carried out using standard sampling methods, sample preparation and determination of the content of pollutants.

A quantitative assessment of the input ($\alpha$,%) of a pollutant into a water body was carried out according to the equation (1):

$$\alpha = \frac{c_c-c_b}{c_c} \cdot 100\%,$$

where $c_c$ is the concentration of the pollutant in the control section, $c_b$ is the concentration of the same substance in the background section.

The discussion used stock materials on the amount of application of mineral phosphorus and nitrogen fertilizers to the catchment area of the river. To find the dependence of surface water pollution on natural and anthropogenic factors, the method of multiple regression was used. Statistical data processing was performed using the Statistica 8.0 software package (StatSoft, USA).

3. Results and discussion
Achieving the goal of the work required a preliminary determination of the background concentration ($C_b$) of pollutants in the water of the river Kazanka, formed under the influence of natural geochemical features of the territory and anthropogenic factors. The background concentration ($C_b$) of a pollutant is understood as a statistically substantiated upper confidence limit for the arithmetic mean content of this substance, calculated with a confidence level of 95% based on the results of hydrochemical observations in a section that is not affected by organized pollution sources. The highest values of the calculated average monthly concentrations of pollutants in the water of the river Kazanka at grounded background stations above the Kazan city line were taken as the main (reference) one [4].

Statistical analysis using one-way analysis of variance and non-parametric data validation using the Wilcoxon rank sum test when comparing monitoring data for the Kazanka River outside the city of Kazan in 2014 and 2016 demonstrated the absence of significant differences in interannual values of water quality indicators with a confidence level of $P = 0.95$, which allows us to combine the data obtained [4]. As a result of research, certain values of the modern geochemical background ($C_b$) of total phosphorus, nitrogen and suspended matter in the Kazanka River were 0.05 mg/L, 1.2 mg/L and 14.5 mg/L, respectively.

Based on the determined $C_b$ values and water monitoring data for the Kazanka River 2014–2017 according to equation (1), the input ($\alpha$,%) of pollutants into the water body is estimated.

Thus, the values of the input ($\alpha$) for nitrogen and total phosphorus into the Kazanka River in the composition of the storm water discharge from the urban area are $35.1 \pm 0.1\%$ and $76.2 \pm 0.1\%$, respectively, therefore, the contribution to the nitrogen concentration in the control sections in the Kazanka River is more than $\frac{1}{3}$ and the total phosphorus concentration is more than $\frac{3}{4}$ due to storm
sewage from the urban area, that is, the organized runoff makes a significant contribution to the increase in the concentration of nutrients in blue-green algae.

Even the most powerful impact on the surface waters of the Kazanka River within the Kazan City is rendered by suspended matter, the concentration of which practically doubles \((a = 95–97\%\) in river water in the control section under the influence of storm runoff outlets. As a result of partial sedimentation at the storm outlet and downstream, it leads to siltation and shallowing of the studied river and stimulates the processes of anthropogenic eutrophication of the water body \([5]\).

The absolute concentration of suspended matter \((345-511 \text{ mg/L})\) in the surface waters of the river, determined during the monitoring the Kazanka River in the Kazan City, which is significantly higher than the known destructive concentrations for zooplankton \((400 \text{ mg/L})\) \([6]\) and phytoplankton \((100 \text{ mg/L})\) \([7]\), may indicate a depressed state of planktonic organisms in the Kazanka River. The concomitant cyanobacterial blooming can cause an additional negative effect on plankton and fish \([8]\), \([9]\).

A significant amount of substances of different nature, including compounds of biogenic elements, enters water bodies from the drainage surface as part of a diffuse (unorganized) runoff with a mud flow of rain and melt water \([2]\), \([10]\).

One of the ways to reduce the diffuse runoff of nutrients into surface waters from the agriculturally developed catchments of the Kazanka River can regulate the load of mineral fertilizers on arable land, taking into account the hydrometeorological features of the territory. Thus, it was shown earlier \([11]\) that the diffuse runoff of priority pollutants - total phosphorus and ammonium nitrogen - from the agrarian-developed territory of the catchment of the Kazanka River is determined by the dose of mineral fertilizers applied to arable land and by the regional hydrometeorological features of the territory.

Of interest is the difference in meteorological parameters that determine the equilibrium concentration of total phosphorus \((C_{P_{\text{total}}}})\) and ammonium nitrogen \((C_{N\text{(NH4+)}})\) in river water according to equations (2) and (3):

\[
C_{P_{\text{total}}} = 1.15 \cdot S_P + 0.08 \cdot T - 0.97 \quad (r_{0.05} = 0.96) \quad (2)
\]

\[
C_{N\text{(NH4+)}} = 0.992 \cdot S_N - 0.003 \cdot R_a - 0.71, \quad (r_{0.05} = 0.95) \quad (3)
\]

where \(S_P\) and \(S_N\) are the amount of phosphorus and nitrogen-containing mineral fertilizers applied to arable land; \(R_a\) – annual amount of atmospheric precipitation, mm; \(T\) – is the average annual temperature, \(^\circ\text{C}\). So, if the value \(C_{P_{\text{total}}}\) is a function of temperature \((T)\) and is not statistically related to the amount of precipitation \((R_a)\), then, on the contrary, the value \(C_{N\text{(NH4+)}}\) is a function of atmospheric precipitation \((R_a)\) in the territory and is not reliably related to air temperature \((T)\). This may be due to the different nature of the migration of phosphorus and nitrogen compounds in the biosphere. The biogeochemical circulation of phosphorus in the environment is sedimentary with a reserve fund in the lithosphere and has a sedimentation orientation; therefore, the mechanism of chemical weathering and an increase in surface runoff from the catchment area under conditions of increasing temperature \([12]\), \([13]\) is more characteristic of phosphorus. Nitrogen, in contrast to phosphorus, is a water and air migrant due to the high solubility of its mineral and volatility of gaseous compounds. The ease of transition from one form to another under the influence of various factors, the intense biotransformation of nitrogen-containing fertilizers in summer determine the activation of the atmospheric nitrogen component and make the quantitative dependence of the change in diffuse runoff with an increase in temperature ambiguous.

On the basis of the obtained regression dependences (2) and (3) with the use of standards for fishery water bodies as the threshold concentration, the maximum permissible ecological load of phosphorus \((\text{MPEL}_P)\) and nitrogen \((\text{MPEL}_N)\) fertilizers on the catchment of the Kazanka River was calculated, which provides a decrease in diffuse runoff from an agro-developed territory to a level that meets the basic environmental requirements for the quality of surface waters under conditions of maximum, minimum and average values of meteorological parameters \(T\) and \(S_N\), typical for the region (table 1).
Table 1. Maximum permissible environmental load of phosphorus- (MPEL_P) and nitrogen-containing (MPEL_N) mineral fertilizers by active ingredient on the agro-developed catchment of the Kazanka River.

| T, °C | MPEL_P, *) active ingredient per hectare | S_s, *) mm | MPEL_N, *) active ingredient per hectare |
|-------|----------------------------------------|------------|----------------------------------------|
| T_{max} *) | 150 | S_{max} | 420 |
| T_{mean} *) | 180 | S_{mean} | 330 |
| T_{min} *) | 220 | S_{min} | 150 |

Note. *) Explanation in the text.

The use of a new generation of biological products with a reduced migration capacity as a mineral fertilizer can also be promising for reducing the load of mineral fertilizers on an agriculturally developed watershed [14].

4. Conclusion

The considered processes of organized and diffuse runoff from watersheds are practically uncontrolled sources of surface water pollution by the main pollutants – compounds of biogenic elements and suspended matter, initiating anthropogenic eutrophication of a water body, leading to siltation and shallowing of water bodies and are responsible for disrupting ecosystem ties, for replacing dominant species of hydrobionts – “producers” of natural water, for the decline in biodiversity, the risk to public health and the safety of hydraulic structures.

References

[1] Nikitin O V, Stepanova N Yu and Latypova V Z 2015 *Water Science and Technology: Water Supply* 15 693–700
[2] Latypova V Z, Shagidullin R R, Safarova V I, Muhametshin F F, Stepanova N Yu, Nikitin O V, Minakova E A and Shaiirova F M 2018 The role of science in providing water management in the Volga basin *Proc. of Int. Conf. “Clean Water. Kazan”* (Kazan: “Novoe Znanie”) pp 72–6
[3] Latypova V Z, Selivanovskaya S Yu, Stepanova N Yu and Minakova E A 2005 *Uchenye Zapiski Kazanskogo Universiteta* 147 159–70
[4] RD 52.24.622-2017. The procedure for calculating the conditional background concentrations of chemicals in water of water bodies to establish standards for wastewater discharges 2017 (Moscow, Rostov-on-Don: Rosgidromet, Gidrokhimicheskii institut Press)
[5] Sabanaev R N, Nikitin O V, Latypova V Z, Stepanova N Yu, Lukoyanov D E, Yakovleva O G, Shagidullina R A, Gorshkova A T and Safiullin R M 2016 *Bulletin of the Technological University* 19 157–60
[6] Bikunova-Shago L 1986 Effect of suspended solids on phytoplankton *Influence of hydromechanized works on fishery reservoirs* (Leningrad: Promrybvod) p 17–20
[7] Gorbunova A V 1986 Influence of the increased content of suspended matter in water on the growth of three cladocerans *Influence of hydromechanized works on fishery reservoirs* (Leningrad: Promrybvod) p 79–81
[8] Nikitin O, Latypova V 2014 Behavioral response of Daphnia magna (Crustacea, Cladocera) to low concentration of microcystin *Proc. Int. Sci. GeoConf. on Surveying Geology and Mining Ecology Management, SGEM* 2(5) 85–92
[9] Stepanova N, Nikitin O, Latypova V and Kondratyeva T. 2018 Cyanotoxins as a possible cause of fish and waterfowl death in the Kazanka River (Russia) *Proc. Int. Sci. GeoConf. on Surveying Geology and Mining Ecology Management, SGEM* 18(5.1) 229–36
[10] Nesterov E, Frumin G, Egorov P and Lyubimov A 2020 *E3S Web of Conferences* 169 01006
[11] Minakova E A, Shlichkov A P, Latypova V Z and Ilyasova A R 2012 Surface flow of biogenic
elements from the agricultural area: the role of climatic factors Regional Environmental Issues 4 55–61 (In Russian)

[12] Wright R F and Dillon P J 2008 Hydrology and Earth System Sciences 12 333-5
[13] Sereda J, Bogard M, Hudson J, Helps D and Dessouki T 2011 Limnologica 41 1-9
[14] Chebotar’ V K, Kazakov A E and Erofeev S V 2004 Biofertilizer production method Pat. of the Russian Federation RU 2 241 692 C2 appl. 11.10.2002, publ. 10.12.2004