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Assessment of the ecological state of Kazan surface waters

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Abstract. The study of the influence of technogenesis on the state of surface waters in urbanized areas is one of the most urgent ecological and social problems. For processing and analysis of hydrochemical indicators of surface water bodies of Kazan for the period 2014–2020 the generally accepted stastical indicators, as well as the methods of multivariate statistics were used. Hydrochemical models were built using the ArcGisMap software package. The data were grouped using the cluster analysis method separately for each hydrological season with the allocation of 6 groups of hydrochemical components in relation to the maximum permissible values. It has been revealed that the minimum technogenic load on the surface waters of the city falls on the spring period. Based on the analysis of the results obtained, an ecological and hydrological assessment of the state of surface waters was carried out. It was showed that the water bodies of Kazan are classified as unfavorable water bodies.

Keywords: surface water, hydrochemistry, cluster analysis, GIS, technogenesis, monitoring

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Introduction

In connection with the growth of cities and the concentration of the population in a relatively small area, hydrological and hydrogeological studies have recently acquired relevance. These studies are associated with the study and assessment of technogenic factors of changes in the composition of the hydrosphere in industrial-urbanized territories and the study of the transformation of a natural hydrosphere into a natural-technogenic and technogenic one (Sungatullin, 2010; Sungatullin, Khaziev, 2009). Industrial and transport activities (Nikitin et al., 2011), the discharge of urban wastewater (Shagidullin, 2011) lead to the pollution of the urban ecosystem as a whole. The United Nations clearly emphasizes the challenge: “By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally” (United Nation, 2017). The study of the chemical composition of surface waters makes it possible to assess the consequences of human activity on the surface hydrosphere (Kondratyeva, 2013c; Maslov et al., 2015).

The city of Kazan is located on the left bank of the Volga River (Kuibyshev reservoir). Within the boundaries

of the city, 2 zones are distinguished according to the relief hypsometry. The first geomorphological zone is a terraced accumulative undulating plain with absolute elevations of 53–130 m, which occupies most of the city on the Volga and Kazanka coasts and within the lake basins. The minimum absolute elevations (53–56 m) are confined to the banks of the Volga and Kazanka rivers (Fig. 1). The second zone is characterized by absolute elevations up to 180–196 m and is represented by a hilly plateau-like erosion-denudation low plain with a dense network of ravines and gullies.

The area of Kazan is 614.16 km², of which 72.25 km² (8.5%) falls on surface water bodies (rivers, lakes, swamps). Kazanka River (left tributary of the Volga River) has the following tributaries: Solonka, Sukhaya reka, Kinderka, Noksa. The largest surface water body is the Kaban lake system, which consists of three basins: Nizhny Kaban, Sredny Kaban and Verkhny Kaban. Currently, more than 80% of water supply in Kazan is carried out from a surface source – the Volga water intake on the shore of the Kuibyshev reservoir.

In the annual cycle of fluctuations in the level of surface water hydraulically connected with the Kuibyshev reservoir, there are three periods associated with spring filling, summer-autumn relatively stable position and autumn-winter drawdown of the reservoir. The average duration of the spring filling stage is 66–72 days (on average, from April 10 to June 15). The average intensity of the level growth during the period of filling is 16–19 cm/day, the average increase by the end of the

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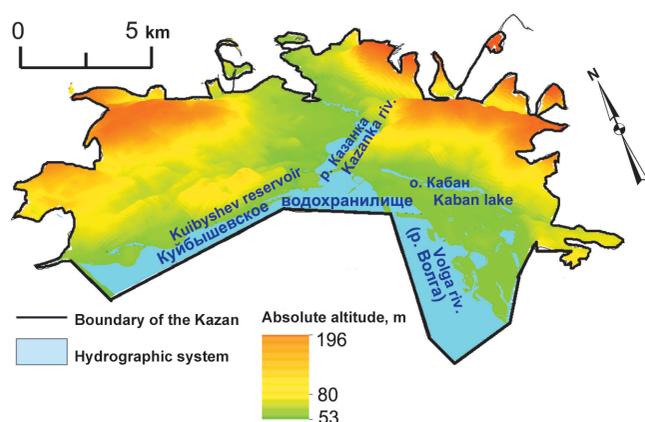


Fig. 1. Relief of the city of Kazan

period is 4.9–5.6 m. For the period of summer-autumn stabilization of the Kuibyshev reservoir lasting 123 days (from June 15 to November 15), a slight change in level is a characteristic. By the end of the period, the level usually decreases by an average of 0.6 m, in some years by 1.3–1.8 m. During the autumn-winter drawdown, the level decreases by 4–5 m, less often to 6.8 m in 176–177 days. The annual amplitude of the change in the level of the Kuibyshev reservoir averages about 6 m.

Pollution entering surface water bodies is associated with different natural causes for certain hydrological cycles. Therefore, during the freeze-up period, groundwater is mainly responsible for surface water pollution; in spring floods, it is solid atmospheric precipitation that accumulates pollutants during the winter months; in the summer-autumn period, pollution associated with rainwater entering the drainage basin, and, in part, the discharge of groundwater. In addition, anthropogenic and man-made activities throughout the year are an important factor in industrial-urbanized areas.

The purpose of this work is to characterize the state of surface waters in Kazan for the period from 2014 to 2020 using the methods of complex assessment zoning of aquatic ecosystems, multidimensional statistical modeling and GIS technologies.

Characteristics of the object and research methods

From geological reports and archival materials, the authors collected the results of 450 winter (freeze-up), 239 spring and 849 summer–autumn series of chemical analyzes of surface waters (reservoir, rivers, lakes, swamps), carried out in the period from 2014 to 2020. The analyzes were carried out according to standard methods within the framework of the monitoring program carried out by the Ministry of Ecology and Natural Resources of the Republic of Tatarstan. We have analyzed data on heavy metals (Cd, Pb, Co, Cu, Ni, Cr, Zn, Mn), phenols, petroleum products, dissolved oxygen content, dichromate oxidizability (COD), inorganic nitrogen compounds (ammonium

ions, nitrate ion, nitrite ion), phosphate ion, chlorides, sulfates, suspended solids.

Statistical processing of analytical data was carried out using MS Excel and STATISTICA software. Methods of basic and multidimensional statistics were used when processing the results of hydrochemical analyzes. The data were divided into three bases according to the hydrograph typical for the rivers of Tatarstan hydraulically connected with the Kuibyshev reservoir for most of the year: freeze-up – winter drawdown, high water and flood – spring filling, summer-autumn low water – a stable level. Only those indicators that contained no more than 20 % gaps in the database were included in the statistical calculations. Before the calculations, the data gaps were restored by averages if the component is required for the water composition, and zeros if the component was a pollutant. The initial points of data grouping were selected based on the criteria for the absence of exceeding the maximum permissible concentrations (MPC).

Cluster analysis refers to the methods of multivariate statistics and identifies classes (clusters) of parameters based on the multitude of variable components of hydrochemical analysis that are more similar compared to objects belonging to other classes. Data clustering was carried out in three stages. At the first stage, the data were ranked relative to the starting point by Euclidean distances and grouped with the condition of forming up to 40 classes; then there were calculated average values of pollution indicators for each class. At the second stage, the agglomerative hierarchical approach of classification by the far-neighbor method (with a grouping of no more than 7 classes) was applied, and the general qualitative characteristics of the members of each class in relation to the MPC were determined; again, the mean values of the pollution indicators for each class were calculated. The clustering process was repeated several times to find persistent datasets. At the third stage, there was plotted a graph of Euclidean distances from the selected starting point to each of the obtained classes. Thus, a large number of the considered water quality parameters were expressed through a smaller number of capacious characteristics convenient for visual perception of the spatial model of the Kazan surface water quality indicators distribution.

In order to construct maps-models of spatial variability of surface water quality indicators in Kazan, the ArcGisMap software package was used, which provides a wide range of different data interpolation methods.

Research Results and Discussion

Due to the low capacity for self-purification, surface waters are subject to significant anthropogenic and technogenic impact. For example, the excess of MPC

in the surface waters of Kazan for the studied period (2014–2020) is recorded for COD and phenols.

COD values in unpolluted water bodies are 2–10 mg O₂/dm³, in slightly polluted – 10–30 mg O₂/dm³, in heavily contaminated ones – from 60 mg O₂/dm³ > and above (SanPiN 2.1.5.980-00). The spatial distribution of the COD of surface waters for 3 hydrological cycles is shown in Figure 2. The average COD values

throughout the study area increases from winter (26.6 mg O₂/dm³) to summer-autumn periods (39 mg O₂/dm³). Increased (more than 60 mg O₂/dm³) COD values were recorded in Lake Verkhny Kaban in winter. It should be noted that the lake is not connected by channels with the Sredny and Nizhny Kaban and is isolated from industrial technogenic impact. The contradictions in the COD indicators of the “technogenic lakes” (Nizhny and Sredny Kaban), where the values are lower in comparison with the Verkhny Kaban lake indicate a positive result of environmental protection measures on the shores of the lake in 2010, when a significant strip of higher aquatic vegetation was cut down. For Kazanka river during the different cycles there is a wide variability of COD values (Fig. 2).

Statistical processing of the surface waters analysis results in Kazan revealed components with exceeding the MPC. Therefore, more than half of winter samples have excess in ammonium, sulfates, phenols; spring and summer-autumn samples contain increased values of sulfates and phenols. Particular attention should be paid to the content of phenols (hazard class 4) in the surface waters of Kazan, exceeding the MPC (0.001 mg/dm³). In the spring (after snowmelt), the content of phenols exceeds the MPC by 5 times, in the summer-autumn and winter periods – by 2 times. There was identified the excess of the MPC (10 times or more) for the COD values.

In order to assess the degree of surface water pollution within the city limits, samples of surface water were analyzed from the most favorable in terms of water quality objects (background territories) – these are lakes Kovalinskoe and Archiereyskoe in Laishevsky district (Table). A critical level of pollution was identified in the system of Kaban lakes and in the old channel of the Kazanka River.

It is worth noting a positive trend in the change in the hydrochemical composition of the Sredny and Nizhny Kaban lakes in the last 8 years. In 2013, a 2-fold excess of maximum allowable concentration was recorded for phenols, oil products and heavy metals (Kondratyeva, 2013a, b). At present, the excess of the MPC for phenols was recorded in the summer-autumn period and amounts to 1.4 MPC, and the excess for oil products and heavy metals was not found.

The results of surface waters analyzes were divided using the cluster method into 6 groups according to hydrochemical parameters relative to MPC (Fig. 3). The zero group (the center of the diagram in Figure 3) includes waters with indicators without exceeding the MPC (the reference group). Group 1 includes waters with insignificant excess of MPC for ammonium, sulfates. Group 2 combines waters with biogenic pollution (high COD values). Group 3 includes water with ammonium and phosphate pollution. Group 4 consists of waters

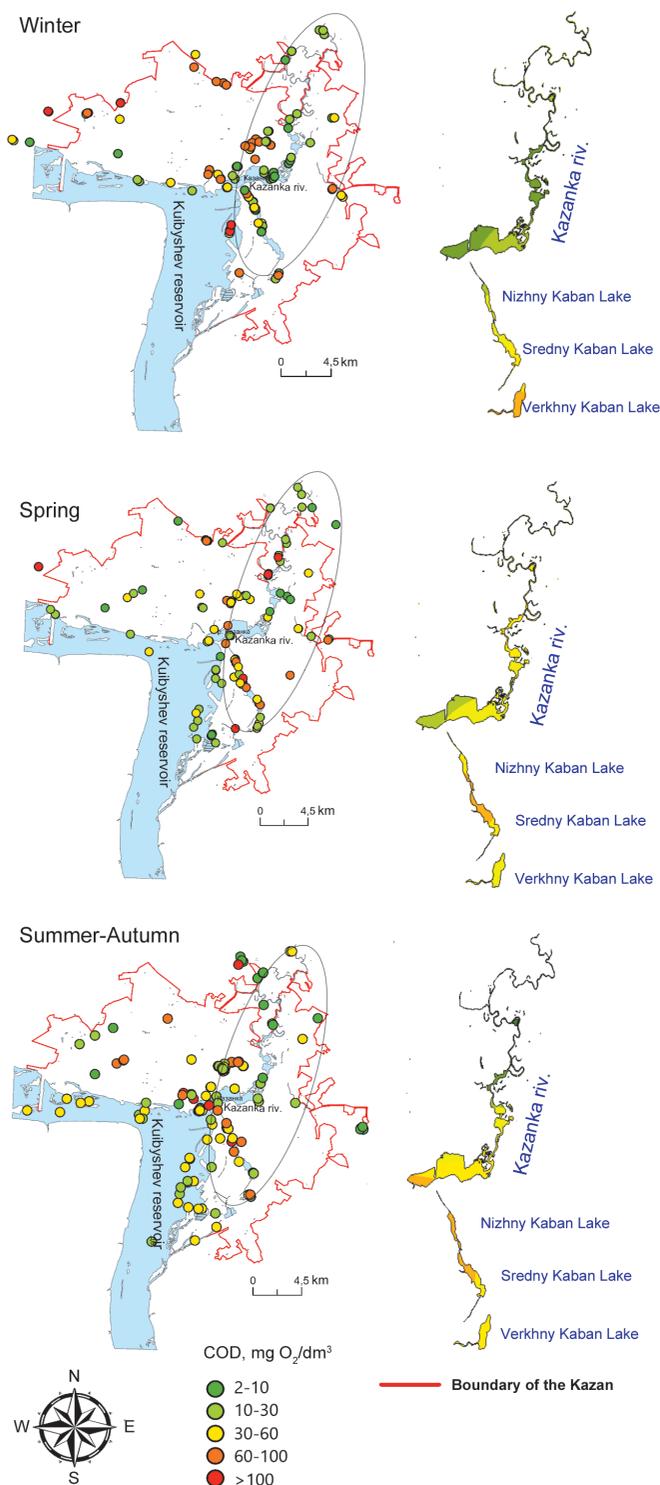


Fig. 2. COD distribution in surface waters. On the left – the places of taking hydrochemical samples and the COD values, on the right – the COD distribution in the Kazanka River and Lake Kaban. Note: n.f. – not found

Indicators. U/M	Lakes Kovalinskoe and Archiereyskoe (Kazan suburbs)			Sredny and Nizhny Kaban Lakes (centre of the city Kazan)		
	Winter	Spring	Summer-Autumn	Winter	Spring	Summer-Autumn
Ammonium ion, mg/dm ³	0.24	0.15	0.05	0.47	0.5	0.36
Dissolved oxygen, mg O ₂ /dm ³	15.93	13.70	13.97	4.2	19	12.68
Petroleum products, mg/dm ³	0.006	N/D	N/D	0.012	0.007	0.11
Nitrite + nitrate, mg/dm ³	1.05	0.08	N/D	8.4	28.9	30
Sulphates, mg/dm ³	3.36	7.26	1.752	341	322.7	349
Phenol, mg/dm ³	0.0001	N/D	N/D	0.0007	0.0001	0.0014
Phosphate ion, mg/dm ³	0.012	0.093	N/D	0.96	0.07	0.08
COD, mg O ₂ /dm ³	18.1	22.0	22.4	55.5	32.7	57
Chlorides, mg/dm ³	5.28	5.74	8.60	116.1	145.5	117.96
TM, mg/dm ³	0.074	0.051	N/D	1.7	0.14	1.7
Number of samples	28	17	42	23	21	39

Table. Average hydrochemical indicators for the lakes by periods

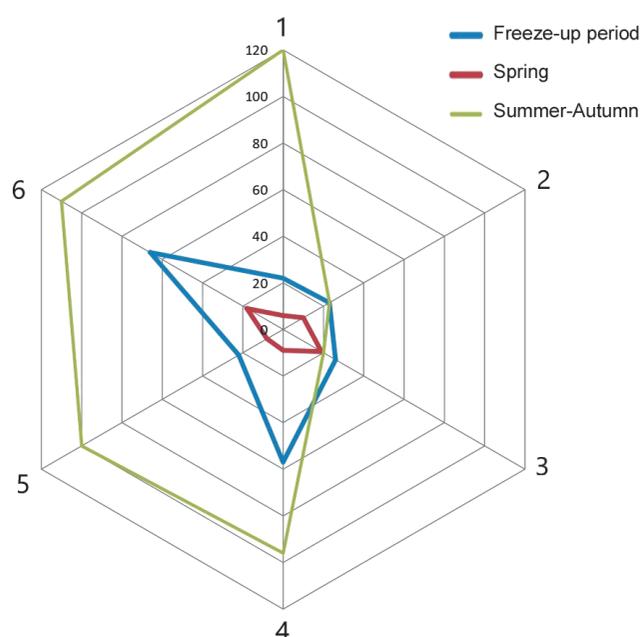


Fig. 3. Euclidean distance from the starting (reference) point to the clusters identified by the hierarchical algorithm

polluted with nitrogen compounds. Group 5 includes waters with exceeding MPC for most components, and Group 6 includes waters with a high content of heavy metals and phenols (technogenic pollution).

The performed clustering of hydrochemical data with distribution over hydrological cycles made it possible to establish (Fig. 4) that intra-annual changes in the content of heavy metals and phenols in the study area reach maximum values during the spring flood (cluster 6). Presumably, this pollution is related to surface washout from the catchment area. In winter, the northern part of the territory is generally safe in terms of surface water pollution with insignificant excess of MPCs for ammonium and sulfates (cluster 1), indicating the influence of groundwater during this period. COD values are higher than the MPC (cluster 2), recorded in the summer-autumn period due to water bloom, and in

the spring – the water of the Kazanka river. There are no completely environmentally safe surface waters on the territory of the city.

Conclusions

1. Using the methods of mathematical statistics and spatial cartographic analysis of hydrochemical information, the state of surface waters of Kazan was characterized for the period from 2014 to 2020.

2. A significant part of surface waters contains high concentrations of sulfates, which is associated with the geological features of the territory.

3. No objects that are completely safe in terms of the chemical composition of surface waters have been found on the territory of the city. It was revealed that the minimum technogenic load on the surface waters of the city falls on the spring. The largest number of excess MPCs is recorded for phenols during the freeze-up period and in the spring, and for phenols, ammonium and phosphates in the summer-autumn period.

4. Using the methods of multidimensional mathematical statistics, it is possible to develop quantitative criteria for identifying and assessing the contribution of technogenic impact on the surface waters of the industrial-urbanized territory of Kazan with the transition to digital monitoring of the city's hydrosphere quality.

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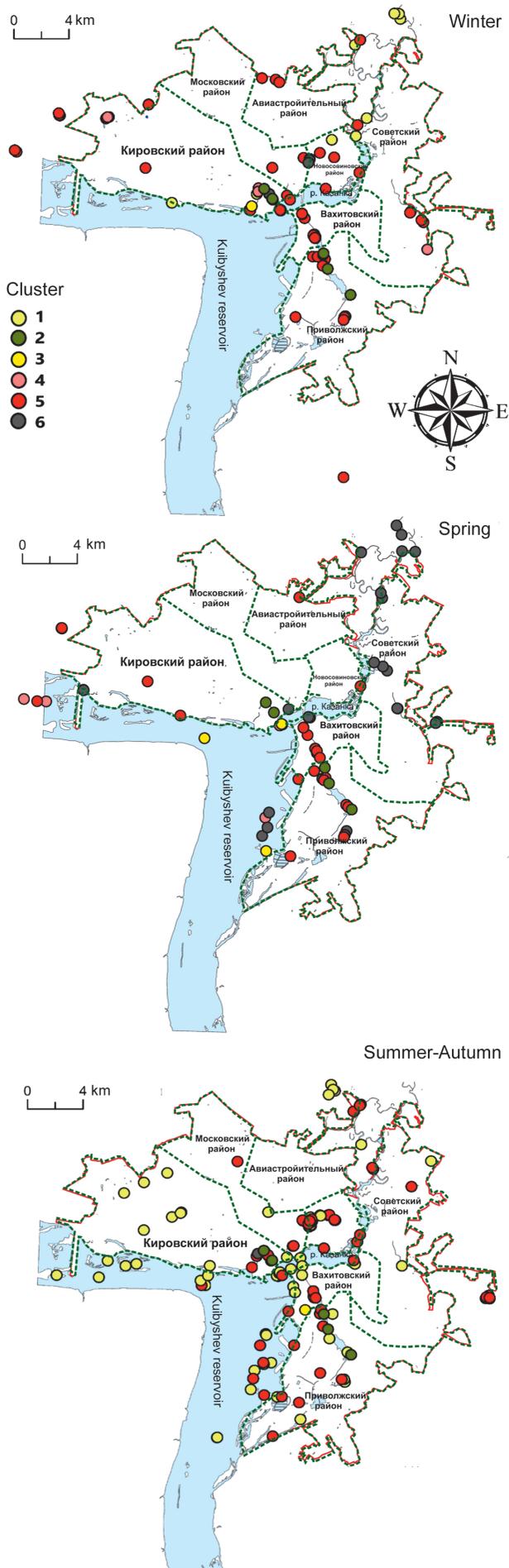


Fig. 4. Clusters of surface water pollution on the territory of Kazan

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