Hydrochemical indicators dynamics of the lakes of Volzhsko-Kamsky State Nature Biosphere Reserve

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Abstract. The article discusses the results of long-term monitoring of the hydrochemical state of different types of lakes in the Raifa part of the Volzhsko-Kamsky State Nature Biosphere Reserve (Republic of Tatarstan). The comparative characteristics of the chemical composition and water quality of flowing and drainless lakes are given, and the multiplicities of exceeding the maximum permissible concentrations of pollutants in the summer period of 2016-2020 are revealed. It is noted that flowing lakes with a swampy catchment area in the Ser-Bulak river valley are most susceptible to biogenic load. High concentrations of heavy metals are associated with the accumulation of organic substances in these reservoirs.

1. Introduction

The process of forming the chemical composition of natural waters is very complex and depends on many factors, including the external flow of substances into lakes with surface and underground runoff, intra-water processes and anthropogenic changes [1]. The natural hydrochemical regime of reservoirs in the region for comparative analysis is studied on reference sites of specially protected natural territories. The Raifa part of the Volzhsko-Kamsky Reserve (Republic of Tatarstan), located on the left slope of the Volga valley, on its high Quaternary floodplain terraces, dissected by the valleys of the Sumka River and its tributaries, numerous hollows and ravines, was selected for research. The surface of the terraces is complicated by karst and karst-suffusion depressions and craters, many of which are occupied by lakes [2]. The territory of the Reserve borders on agricultural land and settlements, which causes anthropogenic changes in the hydrochemical regime of surface water bodies.

On the catchment area of the Raifa part of the Reserve, lakes of different types are connected into a single hydrological system by the small rivers Sumka and Ser-Bulak. By origin, physical and geographical characteristics, the lakes can be divided into groups: flowing lakes of karst-suffusion origin with a maximum depth \( h_{\text{max}} \) of 4.5-20.3 m in river valleys (the lakes Beloe, Raifskoe, Ilinskoe, Linevo, Karasikha), drainless lakes of suffusion origin, \( h_{\text{max}} \) 1.5-3.0 m (the lakes Ilantovo, Krugloe, Mokhovoe, Krutoe, Shatunikha) and “bog window” – the lakes completely surrounded by peat bogs.
(h_{\text{max}} 5.4-12.5 \text{ m}) (the lakes Gniloe, Dolgoe). A beaver pond (h_{\text{max}} 1.5 \text{ m}) (Torfyane Lake) was also investigated.

Monitoring of the hydrochemical state of water bodies and watercourses of the Reserve has been carried out by these organizations for more than 10 years and the main physical and chemical indicators have been published [3,4,5].

This article summarizes the results of hydrochemical studies for 2008-2020, and provides a comparative description of the content of pollutants in flowing and drainless lakes for 2016-2020.

2. Materials and methods
Water samples were collected at a network of control stations in the summer of 2008-2020. The samples were taken from the surface and bottom horizons, or in coastal zone in case of shallow lakes. In total, 120 samples were processed for 24 ingredients, and the physical parameters of water were recorded at time of sampling: transparency (according to the Secchi disk), color (according to the color scale GOST 4266-79), temperature every 2 m (using a thermometer on the Molchanov bathometer). Analytical determination of ionic content and concentrations of the soluble forms of nutrients and metals was performed by optical and atomic absorption spectroscopy using certified methods. Comparison of chemical parameters was carried out in accordance with the maximum permissible concentrations for fisheries reservoirs (MPCr.x.) [6].

The type of water was determined on the scale of O A Alekin [7]. Water quality assessment was carried out according to the method of integrated assessment of the degree of surface water pollution by hydrochemical indicators (RD 52.24.643-2002) with the calculation of the specific combinatorial index of water pollution (UKIZV). The calculation was carried out according to the mandatory list of 15 pollutants with the inclusion of 3 specific substances of local significance (pH, phosphate ion and hydrogen sulfide and sulfides). A preliminary assessment of the degree of water pollution was carried out using the coefficient of complexity of water pollution (K) (a relative indirect indicator of the degree of pollution), which was expressed as a percentage, increasing as the water quality deteriorates. An evaluation score (S) was calculated for each ingredient, taking into account both the values of the observed concentrations and the frequency of their detection. The assessment of lake pollution was carried out separately for near-surface and near-bottom layers due to their varying degrees of contamination.

3. Results and discussions
According to the classification of O A Alekin, the water type of the studied water bodies belonged to the bicarbonate class of the calcium group. The sum of the main ions (\( \sum u \)) (mineralization) varied for groups of lakes from "small" to "high". The minimum average annual values of \( \sum u \) (25.4-27.0 mg dm\(^{-3}\)) were observed in "bog window" lakes, and the maximum values (229.5-347.9 mg dm\(^{-3}\)), in flowing lakes located in the valley of the Sumka River. In drainless lakes, the mineralization value varied in a wide range, from 37.9 mg dm\(^{-3}\) (Ilantovo Lake) to 219.3 mg dm\(^{-3}\) (Mokhovoe Lake). The ratios of the main ions changed slightly in the interannual dynamics for groups of lakes, the highest values were always observed in the bottom layers.

The electrical conductivity of water was 53-74 \( \mu \text{m} \text{cm}^{-1} \) in drainless lakes, and 445-638 \( \mu \text{m} \text{cm}^{-1} \) in flowing lakes.

The pH value varied in a wide range. In flowing lakes, it corresponded to a neutral and slightly alkaline reaction (7.0-8.8) at the surface and varied from weakly acidic (6.9) to slightly alkaline (7.4) at the bottom, which corresponds to MPC.x. In drainless swampy lakes, the pH in the surface layer was neutral, and in the bottom layers it gradually decreased to 6.5, and in the "bog window" lakes to 5.5.

The total hardness of the lake water was characterized as "soft" (less than 4.0 mmol dm\(^{-3}\)), and in some periods in the flowing lakes of the Sumka River, it increased to "medium" (5.9-6.9 mmol dm\(^{-3}\)).

The gas regime was characterized by normal oxygen saturation in the surface layers of all lakes; the concentration of dissolved oxygen varied in the range of 6.5-17.9 mg dm\(^{-3}\). However, in the bottom
layers of flowing lakes located in the Ser-Bulak River valley and in the "bog window" lakes, the deficit of O₂ was observed even in summer (1.0-5.4 mg dm⁻³). These lakes are characterized by the accumulation of hydrogen sulfide and sulfides at the bottom layers in concentration of 0.14-0.27 mg dm⁻³ (up to 74 MPCr.x.).

The level of biogenic load and the amount of organic substances (in terms of BOC₃ and COD) differed in each reservoir. BOC₃ averaged 1.3-8.5 mgO₂ dm⁻³ at the surface layers and 2.2-6.9 mgO₂ dm⁻³ at the bottom layers (4.2 and 3.5 MPCr.x.), COD was 21-75 and 10.6-85 mgO₂ dm⁻³, respectively (up to 2.8 MPCr.x.). During the research period, the highest values of organic matter content were recorded in the Lake Krutoe (table 1).

### Table 1. Content of organic and biogenic substances in the water of the studied lakes

| Lake    | BOD₃, mgO₂ dm⁻³ | COD, mgO₂ dm⁻³ | NH₄⁺, mg dm⁻³ | NO₂⁻, mg dm⁻³ | NO₃⁻, mg dm⁻³ | PO₄³⁻, mg dm⁻³ |
|---------|----------------|----------------|---------------|---------------|---------------|---------------|
| MPC r. x. | 2.0            | 0.5            | 0.08          | 40.0          | 0.7           |
| Beloe   | 2.10±0.30      | 12.7±3.6      | 0.05±0.99     | 0.02±0.11     | 0.1±1.0       | 0.05±0.26     |
| Raifskoe| 4.13±1.35      | 25.6±6.3      | 0.36±0.22     | 0.04±0.03     | 0.43±0.36     | 0.10±0.06     |
| Ilinskoe| 1.20±2.59      | 13.7±24.0     | 0.05±1.32     | 0.02±0.26     | 0.1±1.3       | 0.05±0.14     |
| Linevo  | 4.11±1.38      | 17.1±5.2      | 0.58±0.45     | 0.07±0.06     | 0.48±0.47     | 0.09±0.04     |
| Karasih | 2.25±3.96      | 49.9±77.0     | 0.39±8.30     | 0.02±0.04     | 0.1±1.0       | 11.3±2.0      |
| Krugloe | 3.02±0.45      | 57.1±6.1      | 2.13±1.60     | 0.02±0.00     | 0.19±0.16     | 1.10±0.96     |
| Ilantoi | 1.19±2.0      | 58.7±4.7      | 1.36±0.67     | 0.02±0.00     | 0.18±0.14     | 0.60±0.43     |
| Kugloe  | 3.26±1.48      | 48.3±7.3      | 0.42±0.22     | 0.02±0.00     | 0.1±0.0       | 0.05±0.01     |
| Mohovoe | 3.33±1.5      | 31.1±4.7      | 0.31±1.12     | 0.03±0.01     | 0.1±0.0       | 0.05±0.00     |
| Dolgoe  | 4.44±1.26      | 45.9±4.6      | 1.11±0.77     | 0.02±0.00     | 0.17±0.11     | 0.35±0.31     |
| Gniloe  | 3.37±0.6      | 47.9±5.6      | 0.33±1.38     | 0.02±0.02     | 0.1±0.0       | 0.04±0.05     |
| Shatunih| 3.45±0.5      | 85.1±108.0    | 0.44±13.20    | 0.02±0.02     | 0.1±17.50     | 0.04±2.50     |
| Krutoe  | 3.80±0.85     | 73.7±59.0     | 0.15±0.55     | 0.02±0.05     | 0.1±0.37      | 0.05±0.11     |
| Torfanoe| 3.50±0.61     | 47.5±63.0     | 0.29±11.9     | 0.02±0.02     | 0.1±0.0       | 0.05±0.00     |
| Torfanoe| 2.51±0.90     | 43.9±12.8     | 0.50±3.61     | 0.02±0.02     | 0.1±0.83      | 0.25±0.79     |

* Above the line, the minimum and maximum values; below the line, the average±SD. The maximum values are detected in the bottom layers of the lakes.

Among the biogenic elements, the greatest influence was exerted by the concentrations of ammonium ion and phosphate ion, the concentrations of nitrates and nitrates often corresponded to analytical zero or did not exceed 0.02-0.32 mg dm⁻³ NO₂⁻ and 0.14-0.97 mg dm⁻³ NO₃⁻ throughout the water column.

The phosphate ion content in the surface layers of all lakes was no more than 0.05 mg dm⁻³, in the bottom layers it varied in a wide range and was 0.06-0.18 mg dm⁻³ in the flowing lakes of the Sumka River, 0.6-3.2 mg dm⁻³ in the flowing lakes of the Ser-Bulak River, and 0.39-0.40 mg dm⁻³ in the drainless lakes. The exception was the Lake Gniloe (0.86-2.3 mg dm⁻³ of PO₄³⁻). The multiplicity of exceeding MPCr.x. was 11.5-16.
The variability of the concentration of mineral forms of nitrogen and phosphorus for different types of lakes is shown in figure 1.

![Figure 1](image-url)

**Figure 1** Comparative characteristics of the content of mineral forms of nitrogen and phosphorus in flowing (A) and drainless lakes (B) of the Reserve according to the average data for 2016-2020.

In swampy lakes, high values of phenol content (46 MPCr.x.) are noted, especially in the bottom horizons, which may be due to the large amount of colored humus substances coming from the
catchment area. Consequently, the contribution of phenols to the pollution index might be due to
natural causes in addition to anthropogenic ones.

Heavy metal concentrations were within normal limits, with the exception of copper, manganese,
and iron. In different years, the excess of MPCr.x. was 1.6-3.4 times for copper, 5.1-56 times for
manganese, and 4.8-74 times for iron; the maximum values were observed in the bottom layers of
the Lake Linevo. In swampy lakes, these indicators have always been higher, which is associated with
acidification and accumulation of easily soluble organic forms, which contributes to the formation of
soluble metal compounds. It was metals that determined the assessment of water quality.

The results of calculating the specific combinatorial index of water pollution (UKIZV) showed that
the lake water quality varied from "dirty" (quality class 4a) to "extremely dirty" (quality class 5)
(figure 2). The average coefficient of complexity varied from 10 to 80%.

According to the generalized assessment score (S), the worst of water quality parameter was BOD5;
its S values exceeded 9 in the flow-through lakes Ilyinskoe and Linevo and in almost all drainless
lakes. In all the studied lakes, high S values were found for phenols and several metals, i.e. iron,
copper, and manganese. In flow-through lakes of Ser-Bulak River, elevated S values for such nutrients
as ammonium and phosphate ions were registered. In these lakes, the UCISV values were higher than
in all other lakes of Raifa part (figure 2). Contamination of the bottom layers of lakes was high and
belonged to the quality class 5 "extreme dirty water". It should be noted that this method of water
quality assessment does not take into account the geochemical features of the surface waters of the
region, i.e. the high background content of manganese, copper and iron, and gives an overestimated
value, which is not typical for protected lakes.

![Figure 2. Evaluation of contamination of the waters of the lakes of the Volzhsko-Kamsky Reserve according to 2008-2020 data. The x-axis lists the names of lakes, y-axis – values UKIZV.](image-url)
4. Conclusion
Long-term changes of hydrochemical state of the lake Raif part of the Volzhsko-Kamsky Reserve and its buffer zone indicates the reduction of pollution of flowing lakes occurring in the last decade due to a decrease of the total volume of runoff and a reduction in the intensity of agricultural production in its buffer zone. A decrease in the eutrophication of lakes is observed. The concentration of ammonium and phosphate ions decreases in the surface horizons of all lakes; however, high values remain in the bottom horizons of swampy flowing and some drainless lakes. In general, the water quality of the lakes of the Reserve is higher than in reservoirs outside its borders experiencing direct anthropogenic impact.

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