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# Features of the winter hydrochemical regime of the upper Volga Reservoirs

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**Abstract.** This article presents the results of a study of the winter hydrochemical regime of the reservoirs of the Upper Volga basin. It has been found that in winter, when there is water drawdown and a decrease in the volume of water, the concentrations of the main ions, nutrients, heavy metals, and oil products increase in comparison with other seasons of the year. Water masses of the Upper Volga reservoirs are characterized by low hardness, neutral pH and low chromaticity. Also noted was an increasing concentration of hydrocarbonates towards the bottom.

## 1. Introduction

The winter regime of reservoirs is the set of processes active in forming the water level regime and the associated changes in morphometric characteristics of the bed amidst the formation, development and destruction of ice formations under the influence of natural and anthropogenic factors in the period of negative temperatures [1].

Seasonal regulation of reservoirs is characterized by a decrease in the water level in the winter season. At the beginning of winter the source of water flow transforms from mainly surface and ground sources to underground inflows, and at the end of the season the reverse transition, back to surface and ground inflows, occurs. The time interval of this period is determined by a steady drop in temperatures to below 0°C in the autumn through a rise back to positive temperatures in the spring [2].

The winter hydrochemical regime of bodies of water and watercourses is formed during the process of ice cover. This period is characterized by low water temperature, the absence of surface water flow, the prevalence of groundwater feed, water drawdown in reservoirs, a change in the nature of chemical element migration in water, a limited oxygen supply, and a decrease in aquatic biota activity.

Despite the ice cover, water mixing and a slow current occur under the ice. [3]. Due to the absence of surface water flow and ice formation, the volume of water decreases and there is a concentration of mineral substances.



## 2. Materials and methods

Study of the hydrochemical regime in the winter period of 2017 and 2018 was conducted at the stretch of the Upper Volga from the Upper Volga Reservoir to the upper pool of the Uglich Hydroelectric Power Plant (Figure 1). The Vyshny Volochyok Reservoir was also studied.



**Figure 1.** Map-diagram of the Upper Volga basin with observation stations:

Legend: 1 – Upper Volga Reservoir/Peno settlement, 2 – Upper Volga Reservoir/Selishche village settlement, 3 – Volga River/Ryabeevo village, 4 – Volga River/Gorokhovo village, 5 – Ivankovo Reservoir/Gorodnya village settlement, 6 – Ivankovo Reservoir/Staroe Melkovo village, 7 – Ivankovo Reservoir/Bezborodovo village, 8 – Ivankovo Reservoir/city of Konakovo, 9 – upper pool of the Ivankovo Hydroelectric Power Station, 10 – Uglich Reservoir/city of Dubna, 11 – Uglich Reservoir/city of Kimry, 12 – Uglich Reservoir/urban-type settlement Bely Gorodok, 13 – Uglich Reservoir/city of Kalyazin, 14 – Uglich Reservoir/Priluki village settlement, 15 – upper pool of the Uglich Hydroelectric Power Plant, 16 – Vyshny Volochyok Reservoir/mouth of the Shlina River, 17 – Vyshny Volochyok Reservoir/Krasnomaisky settlement, 18. Vyshny Volochyok Reservoir/city of Vyshny Volochyok, 19. Vyshny Volochyok Reservoir/beginning of the Novo-Tveretsky Canal.

Water samples for hydrochemical analysis were taken from the surface layer in accordance with GOST 3161-2012 “Water. General requirements for sampling.” Chemical analysis of the samples was conducted in the accredited chemical laboratory of the Ivankovskaya Research Station, a branch of the Institute of Water Problems of the Russian Academy of Sciences, according to conventions. The following parameters were determined in water samples: pH, turbidity,  $\text{HCO}_3$ , Ca, Mg,  $\text{SO}_4$ , Cl, Na and K, Fe, Mn, Si, compounds of N and P,  $\text{BOD}_5$  (biochemical oxygen demand), permanganate oxidability, chromaticity, oil products, synthetic surface-active substances, Zn, Pb, Cu, Cr.

## 3. Results

In the Upper Volga Reservoir concentrations of hydrocarbonates in winter amounted to  $92 \text{ mg/dm}^3$ , at the Volga River/Ryabeevo village station (upstream from the city of Tver) they amounted to  $159 \text{ mg/dm}^3$ . They varied from 153 to  $241 \text{ mg/dm}^3$  in the Ivankovo Reservoir, and from 153 to  $177 \text{ mg/dm}^3$  in the Uglich Reservoir.

Water mineralization changed from  $134 \text{ mg/dm}^3$  (Upper Volga Reservoir) to  $265 \text{ mg/dm}^3$  (the upper pool of the Uglich hydroelectric power plant). In the Vyshny Volochyok Reservoir water mineralization amounted to  $140 \text{ mg/dm}^3$ .

Concentrations of calcium and magnesium in the Ivankovo and Uglich reservoirs amounted to 55 and 42 mg/dm<sup>3</sup> and 16 and 13 mg/dm<sup>3</sup>, respectively. In the winter period, chloride concentration increases further down the Volga River: 0.6 mg/dm<sup>3</sup> (Upper Volga Reservoir), 4.2 mg/dm<sup>3</sup> (Volga River/Ryabeevo village, upstream from the city of Tver), 4.5-6.7 mg/dm<sup>3</sup> in the Ivankovo Reservoir and 5.1-6.4 mg/dm<sup>3</sup> in the Uglich Reservoir; sulfates: 7.8 mg/dm<sup>3</sup> (Upper Volga Reservoir), 7.9 mg/dm<sup>3</sup> (Volga River/Ryabeevo village, upstream from the city of Tver), 12.8 mg/dm<sup>3</sup> (Volga River/Gorokhovo village, downstream from the city of Tver), 8.5-14.1 mg/dm<sup>3</sup> in Ivankovo and 7.3-18.9 mg/dm<sup>3</sup> in Uglich reservoirs. Concentrations of sodium and potassium varied in the range of 1.1 mg/dm<sup>3</sup> to 12.5 mg/dm<sup>3</sup>.

Concentrations of total soluble phosphorus grow by 0.013 mg/dm<sup>3</sup> downstream from the city of Tver in comparison to the Upper Volga Reservoir, changing in the reservoirs located below in the range of 0.063-0.093 mgP/dm<sup>3</sup>. Concentrations of mineral phosphorus in the Uglich Reservoir amount to 0.042-0.055 mgP/dm<sup>3</sup>, concentrations of total gross phosphorus in the upper pool of the Uglich hydroelectric power station amount to 0.126 mg/dm<sup>3</sup>.

In winter concentrations of nitrogen compounds grow from the source to the city of Tver (Ryabeevo village) twofold (to 0.5 mgN/dm<sup>3</sup> of ammonium nitrogen and nitrates). Downstream from the city of Tver concentrations of nitrates amount to 0.75 mgN/dm<sup>3</sup> (Gorokhovo village) and to 0.14-0.68 mgN/dm<sup>3</sup> at other stations of the Ivankovo Reservoir and at stations of the Uglich Reservoir.

The winter period is characterized by the undersaturation of water with oxygen in surface aquifers and a deficit of oxygen near the bottom. This is noted by some authors [4, 5, 6]. In the Ivankovo Reservoir in the surface aquifer percentage of oxygen saturation amounts to 50-62%, except for Bezborodovo village (7% O<sub>2</sub>). In the Uglich Reservoir high concentrations of ammonium ion are noted at all observation stations (up to 0.58 mgN/dm<sup>3</sup>). Percentage of oxygen saturation amounted to 49% at the Dubna station.

The values of BOD<sub>5</sub> change from 0.7 (Upper Volga Reservoir) to 3.0 mgO/dm<sup>3</sup> (upper pool of the Uglich hydroelectric power plant).

The chemical composition of water in the mouth of the Shlina River (Vyshny Volochyok Reservoir) is characterized by low concentrations of sulfates (3.1 mg/dm<sup>3</sup>), chlorides (3.9 mg/dm<sup>3</sup>), sodium and potassium (6.5 mg/dm<sup>3</sup>) and biogenic elements (0.040 mg/dm<sup>3</sup> of total soluble phosphorus and 0.14 mg/dm<sup>3</sup> of nitrates).

Concentration of synthetic surface-active substances in water of the Upper Volga and its reservoirs in winter change in the range from 0.005 to 0.045 mg/dm<sup>3</sup>, maximum values are noted in the Ivankovo Reservoir near Gorodnya village settlement and Bezborodovo village, in the Uglich Reservoir near the city of Dubna (0.037 mg/dm<sup>3</sup>) and in the upper pool of the Uglich hydroelectric power plant (0.045 mg/dm<sup>3</sup>). The appearance of thaw holes and increased concentrations of oil products found at the Ivankovo Reservoir stations can be attributed to the Moscow-St. Petersburg highway running through the area: Gorodnya village settlement (0.037 mg/dm<sup>3</sup>), Staroe Melkovo village (0.089 mg/dm<sup>3</sup>), Bezborodovo village (0.036 mg/dm<sup>3</sup>). In the Uglich Reservoir concentrations of oil products are high at all observation points (0.022-0.091 mg/dm<sup>3</sup>), except for the city of Kimry (0.010 mg/dm<sup>3</sup>).

Measurement of heavy metals was conducted in water samples taken in the Ivankovo and Uglich reservoirs. Zinc concentrations higher than MAC<sub>fish.</sub> (0.02 mg/dm<sup>3</sup>) in the Ivankovo Reservoir are noted at the following stations: Staroe Melkovo village (0.0449 mg/dm<sup>3</sup>), Bezborodovo village (0.0593 mg/dm<sup>3</sup>) and city of Konakovo (0.0310 mg/dm<sup>3</sup>); in the Uglich Reservoir: the city of Dubna (0.0208 mg/dm<sup>3</sup>) and in the upper pool of the Uglich hydroelectric power plant (0.0343 mg/dm<sup>3</sup>). In comparison to other seasons, concentrations of zinc in reservoirs in winter are usually lower. Concentrations of copper vary in water in the Ivankovo Reservoir from 0.0033 to 0.0065 mg/dm<sup>3</sup>, and in the Uglich Reservoir the maximum copper concentrations at Kimry amounted to 0.0112 mg/dm<sup>3</sup>, and in the upper pool of the Uglich hydroelectric power plant to 0.0088 mg/dm<sup>3</sup>.

#### 4. Discussion

The main characteristics that determine the freezing process in reservoirs are heat exchange and turbulent mixing, which determine the nature, timing, and duration of the freezing process [7].

By the beginning of the transition of air temperature to negative values, the heat storage of water masses in water reservoirs is greater than in natural rivers due to an increase in depth and a decrease in the flow velocity in the reservoirs backwater zone, and therefore ice appears later [7].

According to meteorological data [8], freezing of the Upper Volga reservoirs starts in early- to mid-November (November 21-22 in 2017-2018, 10-20 November in 2018-2019 in the cities of Ostashkov, Tver, Dubna, Uglich). Ice clearance occurs in early to mid-April at the Vyshny Volochyok Reservoir and in late April at other (March 18-22 in 2017-2018, March 7 in 2018-2019, in the cities of Ostashkov, Tver, Dubna, Uglich). Freezing of reservoirs results in deficit of oxygen near the bottom.

According to results of the previous studies [1-3], the highest concentrations of calcium, magnesium, hydrocarbonates, chlorides and sulfates can be noted in winter runoff, which has been confirmed by our studies.

It has been established that the water is of the hydrocarbonate-calcium type.

Acidity of water medium is characterized by neutral (6.6 pH units near Bezborodovo village (Ivankovo Reservoir) and 7.0 pH units in the Upper Volga Reservoir) and alkaline (up to 7.8 pH units in the upper pool of the Uglich hydroelectric power plant) water types. According to degree of hardness, water is "soft" in the Upper Volga and Vyshny Volochyok reservoirs (up to 2 mg-eq/dm<sup>3</sup>) and is of "average hardness" (up to 3.34 mg-eq/dm<sup>3</sup>) at Ivankovo Reservoir/Bezborodovo village.

With growth of water drawdown of the reservoirs subaquatic discharge grows in the bed and in the sides of groundwater bodies, groundwater being more mineralized in comparison to the surface water. As a result, in the course of decrease of NWL (normal water level) there occurs vertical differentiation of chemical composition of water of the water body. For instance, near the village of Ploski (Ivankovo Reservoir) concentrations of hydrocarbonates (one of the markers of groundwater ingress) grow from surface to bottom by 10 mg/dm<sup>3</sup> at NWL of 123.6 m (January) and by 30 mg/dm<sup>3</sup> at NWL of 122.3 m (February).

Formation of the winter hydrochemical regime of a water body is seriously influenced by the geological and hydrogeological structure of its basin. Whereas mineralization at stations of the Volga branch of the Ivankovo Reservoir in January grows from surface to bottom by 10-20 mg/dm<sup>3</sup>, the difference in mineralization of surface and bottom samples amounted to 40 mg/dm<sup>3</sup> at the Shosha reach (Bezborodovo village), confined to the ancient valleys of the Shosha and Lama rivers.

The transformation of the hydrological regime as a result of flow regulation leads to smoothing of seasonal fluctuations and displacement of the time of passage of extreme concentrations of chemicals. On the extended regulated watercourses the terms of passage of maxima and minima of mineralization are shifted in relation to the passage of similar phases in the riverheads and in relation to what was before the regulation. These shifts are most noticeable during cascade flow regulation. In particular, the maximum mineralization in the upper Volga is observed in early March [11].

An author from Canada [4] notes an increase in the concentration of ammonium, phosphates and a decrease in the concentration of nitrates in winter. This is due to the accumulation of nutrients and the slowing down of biochemical processes, which, despite poor light and temperature, continue in winter [4].

In the winter period the influence of the sewage of the city of Tver on quality of water of the Ivankovo Reservoir is most pronounced; for instance, concentrations of phosphates in water grows [9].

Intra-annual dynamic of concentrations of ammonium nitrogen and nitrate nitrogen is extremely uneven. In the Ivankovo Reservoir concentrations of ammonium nitrogen (0.30-0.44 mgN/dm<sup>3</sup>) and nitrates (0.43-0.62 mgN/dm<sup>3</sup>) in winter period is higher than in other seasons except for Bezborodovo village (0.46 mgN/dm<sup>3</sup> in winter, 0.79 mgN/dm<sup>3</sup> in autumn). This is caused, in particular, by an increased influence of sewage in winter [9].

In natural waters chromaticity is caused mostly by presence of humus substances and ferric compounds [10]. Decrease of chromaticity at the stretch from the Upper Volga Reservoir (100 degrees

on the Pt/Co scale) to the city of Tver (64 degrees) is associated with decrease of the share of swamp inflow in the Volga River. Wetlands flowing into the Upper Volga reservoirs are closely connected with the groundwater (temperature of groundwater in winter amounts to 4-9<sup>0</sup>C), colored water continue flowing in the winter period.

High concentrations of total iron (0.3-0.6 mg/dm<sup>3</sup>) are characteristic for reservoirs of Upper Volga in all seasons. Manganese is introduced by water from the Shosha and Lama rivers to the Ivankovo Reservoir in concentration of 0.31 mg/dm<sup>3</sup>, thus increasing the manganese content fivefold in the Shosha reach of the Ivankovo Reservoir.

According to the integrated assessment of anthropogenic load [12] the calculated water use area on the Shlina River has a high degree of anthropogenic load; on the Tsna River – the average degree of load. The main polluter of surface water in the Vyshny Volochyok District of Tver Region is transport. The volume of wastewater discharge is relatively small.

Low concentrations of the main ions and biogenic elements in water of the Vyshny Volochyok Reservoir can be explained both by natural peculiarities of the drainage basin and by weak manmade load on the water body.

## 5. Conclusions

Water masses of the reservoirs of the Upper Volga basin (Upper Volga, Vyshny Volochyok, Ivankovo, and Uglich reservoirs) in winter are characterized by small hardness, neutral pH indicator, concentrations of hydrocarbonates, calcium, magnesium, sulfates, chlorides, nitrates, phosphates and ion of ammonium, sodium and potassium bigger than in other seasons and low chromaticity of water. Undersaturation of water with oxygen is noted in the surface aquifers and oxygen deficit is noted near the bottom. Increase of concentrations of hydrocarbonates is noted from surface to bottom.

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