Trends in long-term water quality changes in Ivan’kovo and Uglich reservoirs

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Abstract. A comparative analysis of water quality indicators in the upper and lower parts of the Ivan’kovo and Uglich Reservoirs was carried out based on the analysis of long-term monitoring datasets on water quality condition in reservoirs. The observations were performed at the gauging stations of the State Observation Network and Mosvodokanal in the period from the mid-1980s to 2019 and 2004 accordingly. Over a long-term period, all studied hydrochemical indicators except for Zn and SO4 tend to decrease closer to the dam both in the Ivan’kovo and Uglich Reservoirs. Two periods with sufficiently different average values of considered parameters and their dynamics were distinguished for the Uglich Reservoir according to statistical analysis. A high level of pollution in the Uglich Reservoir is mainly associated with heavy metals (Cu, Zn, Fe), phenols and oil products and is typical for both the upper and lower parts of the reservoir. Such pattern is inherent to both heterogeneous periods (1985-2000 and 2001-2019) identified for the Uglich Reservoir. The main trends of long-term and seasonal variability in water quality of the Ivan’kovo and Uglich Reservoirs have been identified using the water pollution index.

1. Introduction

The water quality of the Ivan’kovo and Uglich Reservoirs has been studied previously on many occasions. A significant number of scientific literature is published concerning various studies on hydrochemical characteristics of water and bottom sediments in reservoirs, as well as studies on secondary pollution [1-4]. Among other subjects, the assessment of long-term water quality changes in reservoirs was carried out previously [5, 6]. Long-term changes in water quality indicators resulted from anthropogenic and natural factors were also studied [7]. The problem of water quality of reservoirs is given quite a lot of attention in various regions of the world [8, 9].

The main objective of this study consisted of comparative analysis of water quality indicators in the upper and lower parts of the Ivan’kovo and Uglich reservoirs; estimation of their long-term changes and its correlation with the long-term dynamics of wastewater discharge of different treatment levels; as well as the pollution level analysis for reservoir water compared to maximum permissible concentrations (MPC) of considered hydrochemical indicators and in integral form using a water pollution index (WPI) [10, 11].
2. Materials
The Ivan’kovo and Uglich reservoirs comprise the uppermost part of the Volga reservoir system. Both reservoirs belong to the valley-dammed type, however the Ivan’kovo Reservoir is characterised by a more complex configuration. Both studied reservoirs are approximately equal in their volume (1.12 and 1.25 km$^3$, respectively) and could be described with high water exchange coefficients (8.3 and 9.2, respectively). Seasonal fluctuations in water level in reservoirs are largely determined by the operating mode of the Ivan’kovo and Uglich Water Power Stations and, thus, could reach substantial values of 7 m in the Uglich Reservoir, and 4 m in the Ivan’kovo Reservoir [12].

To analyse the water quality of studied reservoirs, long-term monitoring datasets on water quality at the gauging stations of the State Observation Network (SON) in cities of Dubna (2006 – 2019), Kimry (1985 – 1996; 2006-2015), Kalyazin (1985 – 1996; 2009 – 2015) and Uglich (1985 – 2015) were used. The datasets consisted of annually-averaged concentration values of the following hydrochemical indicators: major ions (HCO$_3$, SO$_4$, Cl, Ca, Mg, Na, K and their sum), heavy metals (Fe, Cu, Mn, Zn, Ni), biogenic elements (PO$_4$, NO$_3$, NO$_2$, NH$_4$) and other (O$_2$, BOD$_5$, COD, pH, oil products, phenols, suspended matter). Additionally, the monitoring data on water quality in the Ivan’kovo reservoir were implemented in the analysis. The observations were carried out by Mosvodokanal at gauging stations Gorodnya and the 1$^{st}$ Ferry crossing and are available for the period 1976 – 2004. This dataset included a long-term series of monthly-averaged concentrations of O$_2$, NO$_3$, NO$_2$, NH$_4$, Cl, SO$_4$, COD, BOD$_5$ and oil products.

Water quality standards for fishery purposes were used to determine maximum permissible concentration (MPC) values [13].

3. Results and discussion

3.1. Spatial variability in long-term averaged concentrations of hydrochemical indicators
All of the considered hydrochemical indicators except for Zn and SO$_4$ could be characterised by a certain decrease in annually-averaged concentration value with the transition from the upper part reservoir to its near-dam zone (table 1). This pattern holds for both the Ivan’kovo and Uglich reservoirs and is observed throughout a long-term period considered in this research. The major ions variability down the longitudinal profile is typical for both studied reservoirs. The largest changes could be observed in concentration values of Cl and Ca (decrease in concentration), and SO$_4$ (increase in concentration). Likewise, the content of biogenic elements changes significantly. Namely, a decrease in the concentrations of nitrogen forms is shown for both reservoirs while phosphates concentrations fall only in the Uglich Reservoir. Thus, the most significant decrease in biogenic elements in the Ivan’kovo Reservoir applies to NH$_4$, while in the Uglich Reservoir it is true for NO$_3$ and PO$_4$. The concentration of some heavy metals changes significantly from the upper reaches of the reservoir to the dam. It could be seen in the Uglich Reservoir as the concentration of Zn increases by 60% and Mn content falls by 37%. Also in the Uglich Reservoir, a substantial decrease (32%) in the concentration of phenols is observed. The concentration of oil products in the Ivan’kovo Reservoir shows a minor decline (by 9%), however a similar tendency in the Uglich Reservoir is even less significant.

3.2. Periods of increased and decreased values of hydrochemical indicators
The analysis of long-term changes in considered hydrochemical indicators has allowed to distinguish 3 separate types of them regarding their temporal variability. The parameters included in the first group experienced a considerable decrease in their concentrations at the beginning of the considered period. It lasted for five to seven years, after which the negative trend smoothed leading to a less intense decline until and it was replaced (approximately at the beginning of the 2000s) with a period of quasi-steady concentrations. In recent years, a minor increase in the concentrations of several elements has been observed. The transition between the indicated periods differs slightly for different hydrochemical parameters. The second type of long-term changes in concentrations represents the
opposite situation compared to the pattern described above. The indicators distributed to the last group could be characterized by the absence of any significant long-term unidirectional changes in concentrations. For those parameters, relatively short-term variability prevailed.

A certain year of trend sign transition was identified using statistical analysis of the long-term data on the Uglich Reservoir water quality indicators (figure 1). This transition happens in both contrasting types of long-term concentrations changes considered above (types 1 and 2).

Table 1. Spatial variability in long-term averaged concentrations of hydrochemical indicators from the upper to a near-dam zone of the Ivan’kovo and Uglich Reservoirs.

| Indicator          | Ivan’kovo Reservoir | Uglich Reservoir |
|--------------------|---------------------|-----------------|
|                    | Gorodnya 1st Ferry  | Kimry           | Uglich          |
|                    | crossing            | Relative        | Relative        |
|                    |                     | difference, %   | difference, %   |
| Suspected matter,  | 7.26                | 6.70            | -7.7            |
| pH                 | 7.72                | 7.67            | -0.6            |
| O₂, mg/l           | 8.60                | 8.49            | -1.3            |
| Mg, mg/l           | 10.37               | 10.12           | -2.5            |
| Ca, mg/l           | 39.98               | 35.63           | -10.9           |
| Cl, mg/l           | 9.24                | 8.45            | -8.5            |
| SO₄, mg/l          | 12.66               | 13.52           | 6.8             |
| HCO₃, mg/l         | 146.78              | 142.92          | -2.6            |
| Sum of ions, mg/l  | 233.63              | 225.49          | -3.5            |
| COD, mg/l          | 28.25               | 28.03           | -0.8            |
| BOD₅, mg/l         | 1.84                | 1.74            | -5.5            |
| NH₄, mg/l          | 0.45                | 0.36            | -19.3           |
| NO₂, mg/l          | 0.018               | 0.014           | -20.6           |
| NO₃, mg/l          | 1.02                | 0.88            | -13.2           |
| Fe, mg/l           | 0.04                | 0.03            | -31.9           |
| Cu, μg/l           | 0.16                | 0.15            | -6.3            |
| Zn, μg/l           | 4.63                | 4.25            | -8.2            |
| Mn, μg/l           | 6.67                | 10.82           | 62.1            |
| Phenols, mg/l      | 0.0016              | 0.0011          | -31.9           |
| Oil products, mg/l | 0.1332              | 0.1209          | -9.2            |

The two periods divided by a transition year could be characterized by a substantial difference in their average values. Furthermore, it could be seen that the variability in mean values of the remaining hydrochemical parameters group (without significant long-term changes; type 3) is extremely small.

A significant decrease in oil products content, as well as a moderate decline in concentrations of Cu, NH₄ and NO₃, was revealed between the two periods. This may have been caused by a reduction in load imposed by agriculture and shipping on the reservoir. The growth of such indicators as Fe, PO₄ and COD could be associated with an increase in the productivity of the reservoir. The growth of organic matter content in the reservoir promotes the formation of anoxic conditions in the bottom layers, which intensifies the flow of Fe and Mn from bottom sediments into the reservoir water. Thus, leading to secondary pollution of the reservoir.
3.3. Correlation between long-term changes of hydrochemical indicators and wastewater discharge

The wastewater discharges of all treatment levels arriving from the catchment into the Ivan’kovo Reservoir are 8-10 times higher than that coming into the Uglich Reservoir [14]. Over the studied period, wastewater inflow to the Uglich Reservoir has been reduced by half from 0.14 to 0.07 km$^3$/year. In the Ivan’kovo Reservoir catchment, the volume of incoming wastewater increased from 1.1 to 1.8 km$^3$/year from 1992 to 2003, after which in 2003-2004 a rapid increase in wastewater discharges happened. Thus, it reached the range of 2-2.5 km$^3$/year in the 2003 – 2014 period.

![Figure 1](image-url)  
Figure 1. The relative difference in mean values of hydrochemical indicators between 1985 – 2000 and 2001 – 2015 periods in the Uglich Reservoir.

It is important to note that the percentage of untreated and insufficiently treated waters in the basin of the Uglich Reservoir was 60-80% over the concerned period, while the same value in the Ivan’kovo Reservoir reached only 10-15%. Beyond that, before the beginning of the 2000s the absolute wastewater discharge value flowing in the Ivan’kovo Reservoir were exceeding the volume of wastewater runoff into the Uglich Reservoir, however the opposite ratio was observed thereafter.

In catchments of both reservoirs, the discharges of untreated and insufficiently treated wastewater have been consistently decreasing during the entire studied period. In the Ivan’kovo Reservoir basin, the reduction rate of wastewater discharges has slightly slowed down after the early 2000s. The same pattern occurred for the Uglich Reservoir, however the pace of decline has returned to normal later. The reduction in the volumes of untreated and insufficiently treated wastewater discharge into the reservoirs has most likely caused the decrease in concentrations of several indicators, such as SO$_4^-$, Cl, NH$_4^+$ and NO$_3^-$ and some others (figure 1).

3.4. Level of water pollution in reservoirs and its long-term changes

The pollution in the Uglich Reservoir comes from heavy metals (Cu, Zn, Fe), phenols and oil products exceeding the maximum permissible concentration (MPC) values on average for a considered long-term period. Moreover, such situation is typical for both the upper and lower parts of the reservoirs. The highest level of MPC exceedance is observed for Cu, Mn and oil products. For them, the multiplier of defined MPC values reaches 4.6, 3.6 and 2.5, respectively. Besides that, although concentrations of these elements decrease closer to the dam (by more than 30% for Mn and phenols),
their excess of MPC remains significant. The exception is Zn, which concentration exceeds the MPC only in the near-dam zone, although the exceedance is hardly noticeable (1.08-MPC).

A similar picture is revealed when comparing the pollution level of the Uglick Reservoir for the two heterogeneous periods considered above (1985 – 2000 and after). For each of them, the greatest excess of MPC is also typical for heavy metals, phenols and oil products. Yet, their concentrations in both the upper and lower parts of the reservoir decreased after 2001 (except Fe and Zn, as well as phenols in the near-dam zone). The most significant reduction in the recent period in both parts of the reservoir was observed for oil products, which fell under the MPC value in the upper part of the reservoir and slightly exceeded it near the dam.

To complete an integral assessment of the water quality dynamics in the Ivan’kovo and Uglick Reservoirs, the water pollution index (WPI) was used. It was calculated in two alternative ways for each year. The first version of the WPI was calculated for all the stations considered using a set of indicators including O₂, NO₂, NH₄, COD, BOD₅ and oil products. The second version used the concentration values of O₂, Mn, Cu, Fe, BOD₅, oil products and phenols (for Dubna station) to perform a water quality estimation for all the stations on the Uglick Reservoir. Such sets of indicators were chosen in line with the existing guidelines [10, 11]. This is primarily due to a general decrease in the concentration of nitrogen forms, as well as of organic matter. According to WPI calculation using version 1, starting from the mid-1980s, a long-term downward trend in pollution level is present (figure 2a).

![WPI graph](image)

**Figure 2.** Variability of WPI coefficient computed using O₂, NO₂, NH₄, COD, BOD₅, oil products (a); and using O₂, Mn, Cu, Fe, BOD₅, oil products, phenols (b) concentration values.

The variability of WPI₁ values (version 1) between different gauging stations could be taken as negligible. However, few extreme values could be observed at stations Dubna and Uglick in 1992 – 1995. According to the WPI₁ computation results, the waters of the Ivan’kovo Reservoir belong to water quality class III, namely “moderately polluted”, before 2002 (WPI₁ 0.6-1.9). After 2002 the water quality class changed to II class or “clean” (WPI₁ 0.5-0.9) for all station except for Dubna (WPI₁ 1.0-1.5).

According to WPI₂ calculations, the water quality of the Uglick Reservoir is assessed as "moderately polluted" (WPI₂ 1.5-3.7; class III) and even "dirty" after 2005 (WPI₂ 4.0-4.4; class IV) (figure 2b). The highest WPI₂ values are bound to the stations of Dubna and Kimry in 2006 – 2009 (WPI₂ 3.6-4.4). This may be associated with an increase in the wastewater discharges volume in the Ivan’kovo Reservoir in 2003 – 2004. Also, it is important to note that with regard to WPI₂ estimates in the lower part of the Uglick Reservoir (in the city of Uglick station, where a continuous series of observations is present), the pattern of long-term changes in water quality differs significantly from that observed when using WPI₁. Following the second version of WPI computation, a series of recurring relatively short-term fluctuations of water quality could be observed over the concerned period. Apparently, such interannual changes in water quality also occurred in other parts of the Uglick Reservoir in a similar way. These fluctuations most likely were caused by a change in
predominant pollutants (hydrochemical indicators that exceeded the MPC) for both the Uglish and, probably, for the Ivan’kovo Reservoirs. Biogenic elements (especially forms of nitrogen) and oil products prevailed until 2000 when due to agriculture intensity reduction, as well as a decrease in the impact of shipping, a noticeable decline in these indicators concentrations occurred. At the same time, after 2000 a significant increase in the concentrations of \( \text{PO}_4, \text{Fe} \), as well as a growth in \( \text{COD} \), \( \text{Mn} \) content at all stations was observed. This may indicate an increase in the productivity of reservoirs, which can intensify the processes of their secondary pollution.

Analysis of long-term changes in monthly-averaged \( \text{WPI}_4 \) values in the upper and lower parts of the Ivan’kovo Reservoir shows that greater values tend to be observed in March and April (1.3 – Gorodnya; 1.05 – 1st Ferry crossing) due to increased inflow of pollutants from the catchment area with snow melt water, as well as at the end of summer (1.3 – Gorodnya; 1.25 – 1st Ferry crossing) due to the higher productivity and blossom in the reservoir at this time of the year. Nevertheless, the highest \( \text{WPI}_4 \) values in the upper reaches of the reservoir are observed both in spring and in summer, while in the lower reaches they are typical for the end of summer.

4. Conclusions

Several conclusions could be drawn based on the analysis of long-term monitoring datasets on the water quality condition in the Ivan’kovo and Uglish Reservoirs. The observations were carried out at the gauging stations of the State Observation Network and Mosvodokanal in the period from the mid-1980s to 2019 and 2004 accordingly. They included a wide range of annually-averaged values of various hydrochemical indicators, including major ions content and its sum, heavy metals, biogenic elements, indicators of organic matter content (\( \text{BOD}_5, \text{COD} \)) and others (\( \text{O}_2, \text{pH} \), oil products, phenols, suspended matter). The major conclusions are as follows:

1. All studied hydrochemical indicators except for \( \text{Zn} \) and \( \text{SO}_4 \) have shown a longitudinal reduction of their concentration values from the upper part of both reservoirs to the zone closer to the dam. Such a pattern was observed considering long-term averaged observation data and could have been less distinct in certain years. This happens due to the effect of internal processes present in reservoirs and the features of anthropogenic impact spatial distribution.

2. Two separate periods were statistically identified within the observations period in the Uglish Reservoir. Generally, the transition between them happened at the start of the 2000s. These periods could be characterised by contrasting types of long-term variability in concentrations of studied parameters leading to significant differences in their average values. However, a few hydrochemical indicators were found to show insignificant unidirectional changes over the years resulting in absence of any distinction between the two periods. Starting from the beginning of the 2000s, a significant decrease in contents of \( \text{Cu}, \text{NH}_4, \text{NO}_3 \) and oil products was observed. This may indicate a decline in agricultural load and the impact of shipping on the reservoir. A significant increase in values of \( \text{Fe}, \text{PO}_4, \text{COD} \) is most likely associated with the productivity growth in the reservoir, which then leads to the promotion of the organic matter content.

3. The long-term dynamics of socio-economic development in the region over the studied period, along with internal processes presented in the reservoirs, have exerted a major impact on the water quality, its pollution level and long-term variability of hydrochemical indicators. This happened due to changes in wastewater discharges (especially untreated and insufficiently treated wastewater) inflowing into the reservoirs in the period from the 1980s to 2010s. The pattern of changes in untreated and insufficiently treated wastewater discharge has affected the reduction of \( \text{SO}_4, \text{Cl}, \text{NH}_4, \text{NO}_3 \) and some other elements content.

4. A high level of pollution by heavy metals (\( \text{Cu}, \text{Zn}, \text{Fe} \)), phenols and oil products (on average over the studied period 1985 – 2019) was found to be typical for both the upper and lower parts of the Uglish Reservoir. A similar picture is revealed while comparing the level of pollution of the Uglish Reservoir for the two heterogeneous periods discussed previously (1985 – 2000 and 2001 – 2019).

A continuous water quality improvement trend starting from the mid-1980s was revealed for Uglish Reservoir according to the integral assessment of long-term water quality transformation.
(water pollution index) based on values of biogenic elements and organic matter contents. However, the pattern of such transformations changes significantly if heavy metals content is used in the calculation of the water pollution index. In this case, relatively short-term recurring periods of water quality deterioration and improvement could be observed over the years considered in this research.

Additionally, according to the water pollution index calculations for the Ivan’kovo Reservoir (without heavy metals impact), a significant decline in water quality is happening in early spring due to an increased pollutants runoff from the catchment area with snow melt water. As well, water quality deterioration, associated with the period of highest productivity and intensified blooming processes, could be observed at the end of the summer. However, it was revealed that while in the upper reaches of the reservoir the highest water pollution index values (calculated without taking into account heavy metals) are observed both in spring and in summer, in the near-dam zone they are mainly common for the end of the summer period.

Acknowledgements
The paper is based on the materials of studies supported by the Russian Science Foundation, project no. 20-17-00209; the methodological approaches have been developed under Governmental Order 0148-2019-0007/AAAA-A19-119021990093-8.

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