Water supply of the population in the cyanobacteria mass development conditions at the Volga reservoirs

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Abstract. The results of the monitoring data analysis of the Kuibyshev reservoir as a source of drinking water supply for the period 2000-2018 are presented. The observations were carried out monthly in the water area and in the closing section of the reservoir, located in the Zhigulevsky dam area. The estimation of temporal variability and spatial heterogeneity of the reservoir water quality is given. It was established that in the summer, during the period of cyanobacteria mass development, biological pollution of the reservoir is observed, the water quality deteriorates by smell, color, pH, and dissolved oxygen content. The content of dissolved organic and toxic substances increases, and the concentration of nutrients, on the contrary, decreases. With a limited concentration of phosphates in the water of the reservoir, the cyanobacteria mass development process stops. In the period of water quality deterioration in the source of water supply in large Volga cities, the problems in the purification of natural water to the requirements of drinking water supply for the population arise. To solve the problem, the recommendations to improve the technological scheme of purification of the Volga water from organic and toxic substances were developed. Organic pollution can be reduced using ozone or activated carbon. Membrane technologies being capable of filtering water and cyanobacterial cells without mechanical damage can serve as a barrier against toxic substances entering drinking water.

Introduction

In many countries of the world the problem of providing the population with high-quality drinking water from surface water sources arises because of the “blooming” of water. As a result of point and diffuse pollution, biogenic substances, in particular nitrogen and phosphorus, enter the water bodies in excessive quantities, which, under conditions of slowed water exchange, cause a massive development of blue-green algae, with a substantial amount of cyanobacteria in them.

Vital activity and death of cyanobacterial cells leads to biological pollution of the water bodies, including toxic substances. The most common toxin is microcystin, which is identified in 79 states [1-3].

There is reason to suppose that an increase in global water temperature due to climate warming will contribute to the cyanobacteria mass development process intensification [4]. In the future, there will be an increase in the duration of the cyanobacteria water and biomass “flowering” period, which will
entail a further deterioration in water quality. Therefore, it is necessary to be prepared for a likely exacerbation of the situation in drinking water supply.

In Russia, the greatest nutrient load is experienced by the water bodies in the Volga basin. On the reservoirs of the Middle and Lower Volga every year during the summer low-water period, there is a massive development of cyanobacteria and a deterioration in water quality by smell, color and organic matter [4, 5]. The most unfavorable conditions for water supply are formed under abnormal hydrometeorological conditions (heat and low water), when there is a likelihood of water pollution not only by organic but also by toxic substances [6].

During the period of “flowering” and a sharp deterioration in the water quality in the water supply source, the water treatment facilities in large Volga cities cannot cope with the purification of Volga water from the organic substances.

Therefore, drinking water periodically does not meet the regulatory requirements for permanganate oxidation [7]. There is evidence of the cyanotoxins discovery in drinking water, which, after purification of the Volga water, enters the city distribution network [8].

To solve the problem, along with protecting water sources from pollution by nutrients, it is necessary to improve the existing processing lines for cleaning the Volga water. The modernization of treatment facilities and the choice of reagents are largely determined by the laws of the water quality seasonal variability in a particular water body.

Materials and methods

The Kuibyshev reservoir is the largest in the Volga-Kama cascade and is characterized by the seasonal regulation of water flow. The reservoir experiences an excessive biogenic load, which in the conditions of slowed water metabolism causes a massive development of cyanobacteria and water quality deterioration.

To study the spatial-temporal changes in water quality, the observational data obtained at the “Biolog” research vessel and at the stationary observation point in the closing section of the reservoir in the period 2000-2018 were used.

The systematic observations were carried out 2.5 km downstream of the Zhiguli dam. The water samples were taken on the left bank of the reservoir monthly with a Molchanov GR-18 bathometer from a depth of 0.5 m. The water samples were filtered through a membrane filter and poured into bottles made of chemically resistant glass with ground stoppers. Before filling, the bottles were rinsed twice with water to be analyzed and filled to the top.

Chemical analysis of water samples was carried out in the laboratory of the Institute of Ecology of the Volga Basin of the Russian Academy of Sciences according to 25 indicators. The main attention was paid to organic substances: permanganate oxidizability (PO) and bichromate oxidizability (BO), as well as nutrients: nitrates (NO\textsubscript{3}^-), phosphate (PO\textsubscript{4}^{3-}).

The software and BO registration was performed by titrimetric, and NO\textsubscript{3}^- and PO\textsubscript{4}^{3-} by the photometric methods. The measurement substances and indicators measured concentrations ranges accuracy are presented in accordance with the current regulatory documents (Table 1).

| Indicators | Range measurements | Guidance document | Accuracy indicator |
|------------|--------------------|-------------------|-------------------|
| PO         | 2.0-100 mgO/dm\textsuperscript{3} | PND F 14.1:2:4.154-99 | ±10% |
| BO         | 10.0-80.0 mgO/dm\textsuperscript{3} | PND F 14.1:2.100-97 | ±24% |
| NO\textsubscript{3}^- | 0.1-3.0 mgN/dm\textsuperscript{3} | PND F 14.1:2.4-95 | ±0.18X mgN/dm\textsuperscript{3} |
| PO\textsubscript{4}^{3-} | 0.01-0.2 mgP/dm\textsuperscript{3} | RD 52.24.382-2006 | ±0.002+0.092X mgP/dm\textsuperscript{3} |

Note: X -denotes the substance concentration

The obtained analysis results were formed in the series that were subjected to statistical processing using the Statistica v 6.0 program. For each water quality indicator for each month, the samples from
19 members of the series (2000-2018) were drawn. These samples were used to determine: the average (C), maximum (C\text{max}) and minimum (C\text{min}) concentration and standard deviation (σ).

**Discussions and Results**

The average annual water discharge in the closing section of the Kuibyshev reservoir is 7674 m$^3$/s, and the range of the seasonal variation – 2100-33500 m$^3$/s. The lowest water discharge is observed during the summer low water period, when favorable conditions are created for the water temperature and flow rate for the mass phytoplankton development.

During the summer low water period, phytoplankton is dominated by blue-green, diatom, and green [9]. It is the blue-green algae, which are cyanobacteria, that cause the “blooming” of water. Every year, when the water temperature rises above 20°C, the process of mass development of cyanobacteria on the reservoir starts. The intensity and duration of the process depends on the magnitude of the nutrient load, the water flow regulation regime and the hydrometeorological conditions of a particular year.

Due to the significant spatial heterogeneity of the water “blooming” process, the number and biomass of cyanobacteria varies over a wide range and amounts to 3-120 million cells/dm$^3$ and 2-25 mg/dm$^3$, respectively. In floodplain parts of the reservoir, the bays, zones of backwater inflows, where there is little depth and flow is practically absent, the water “blooming” is more active than in the channel part. The process is most actively developing in the largest and shallowest Cheremshan Bay, as well as on the dam reach, where the water intake of the city of Tolyatti is located.

During the “bloom” period at the Kuibyshev reservoir, the hydro-chemical regime changes significantly, and the quality of the water deteriorates. In the surface water layer, the oxygen saturation up to 200–300% is observed, and in the bottom layer it is deficient. The smell of water increases to 3-4 points. The color increases to 40-50 degrees.

An alkaline environment is created, a hydrogen indicator (pH) increases to 9–10, and the redox potential (Eh) decreases to 230–250 mV. Biological oxygen consumption (BOC) is increasing, the biomass of cyanobacteria varies over a wide range and amounts to 3-120 million cells/dm$^3$, respectively. In floodplain parts of the reservoir, the bays, zones of backwater inflows, where there is little depth and flow is practically absent, the water “blooming” is more active than in the channel part. The process is most actively developing in the largest and shallowest Cheremshan Bay, as well as on the dam reach, where the water intake of the city of Tolyatti is located.

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Of particular concern is the increased content of the organic substances in water, estimated by such integral indicators as permanganate (PO) and bichromate (BO) oxidizability. The average annual value of software is 7,4 mgO/dm$^3$, and BO - 25,3 mg/dm$^3$. An average (C) monthly software values vary within 7,0–8,6 mg/dm$^3$, maximum (C\text{max}) – 8,6–13,8 mg/dm$^3$, minimum (C\text{min}) – 4,1–7,1 mg/dm$^3$ (Table 2). Intra-annual changes in PO values have a pronounced seasonal variation. The highest average monthly values are observed in the summer low water (July), at the blooming water peak, and the lowest - in the winter low water. Due to the water blooming, PO increases by about 10-15%.

The average monthly values of BO vary within 22,9–27,3 mg/dm$^3$, maximum – 28,9– 38,7 mg/dm$^3$, minimum – 9,5–16,9 mg/dm$^3$. Temporary changes in the concentration of BO have a seasonal course. The highest average monthly values are observed in the summer low water (July), at the peak of flowering water, the lowest - in the winter low water.

| Indicato r | Month | TLV |
|-----------|-------|-----|
|           | 1     | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  |      |
| C         | 7,5   | 7,1 | 7,8 | 7,5 | 7,5 | 7,8 | 8,6 | 7,9 | 7,4 | 7,1 | 7,0 | 7,0 | 5,0** |
| σ         | 1,4   | 1,4 | 1,3 | 1,1 | 1,2 | 1,0 | 1,5 | 1,3 | 1,0 | 1,1 | 0,8 | 0,9 |       |
| C\text{max}| 9,8   | 13,8| 10,7| 10,5| 9,4 | 10  | 12,1| 9,8 | 9,7 | 9,8 | 8,6 | 8,6 |       |
| C\text{min}| 5,5   | 4,1 | 5,2 | 5,4 | 5,8 | 5,5 | 7,1 | 6,5 | 6,2 | 5,9 | 6,0 | 5,3 |       |

**Table 2.** The concentration of permanganate (PO) and bichromate (BO) oxidizability.
The organic substances’ increased content in summer is associated with an increase in the number of autochthonous organic matter due to the intensive development of phytoplankton. The Volga water in terms of PO and BO throughout the year does not meet the requirements for water bodies for household and drinking purposes. In addition, the Volga water during the flowering period does not meet the regulatory requirements for odor, color, pH, dissolved oxygen, BOD₅.

The experience of the treatment facilities in the Volga cities shows that in summer, during the period of mass cyanobacteria development, when the PO values in the water supply source reach 12-16 mg/O/dm³, it is not possible to purify water to a standard quality according to the organic indicators. Therefore, the attempts are periodically made to review the drinking water quality standards in the direction of increasing the concentration of organic substances.

Potential danger to drinking water supply is the special class of cyanobacteria *Microcystis, Anabaena* and *Aphanizomenon*, which are present in the water of the Kuibyshev reservoir and are capable of producing cyanotoxins. They are enclosed in cell walls and exist intracellularly in the cytoplasm or can be released by isolation, destruction of cells, that is, they become extracellular toxins.

The most toxic substance is microcystin-LR, which can enter the human body along with drinking water. Therefore, the World Health Organization (WHO) has established an approximate allowable concentration of microcystin-LR in drinking water no more 1 mcg /dm³ [11].

The intensity and duration of the cyanobacteria mass development is largely determined by the hydrometeorological conditions. In the summer of 2010, abnormal weather conditions (heat and low water) were favorable in the Volga region favorable for the mass development of cyanobacteria. In August, water consumption decreased by three times and amounted to 2175 m³/s. The stock flow was minimal. The average monthly water temperature in the summer months (July, August) increased by 1,1-3,5°C. The highest average monthly water temperature was observed in July and amounted to 23,5°C.

An analysis of the water and temperature regimes of the reservoir showed that in 2010 the most favorable conditions were created for the blue-green algae mass development due to an increase in water temperature and a decrease in the water masses dynamics.

In summer, the algae biomass increased several times. The concentration of chlorophyll “A” increased: in June - from 2,7 to 4,9 mg/m³, in July - from 1,0 to 8,6 mg/m³, in August - from 1,7 to 6,6 mg/m³.

In abnormal 2010, there was a sharp deterioration in water quality by smell, color, pH, and suspended and dissolved organic substances. The concentration of nitrates and phosphates in the reservoir water during the summer period sharply decreased.

At the very peak of “blooming”, the concentration of nitrates decreased to 0,11 mgN/dm³, the phosphate concentration - to 0,010 mgP/dm³. The calculations showed that the consumption of nutrients by algae increased four times. Consequently, the implementation of the global warming scenario will intensify the mass development of cyanobacteria and deteriorate water quality.

In Russia, three classes of water quality are determined for surface sources of drinking water supply, corresponding to three typical technological lines for water treatment, which are determined by the mandatory disinfection (GOST 2761-84). The results of the Volga water quality studies show that during the “blooming” period of water, the Kuibyshev reservoir should be classified as class III in quality (Table 3), given the significant range of seasonal changes in the maximum (Cₘₐₓ) and minimum (Cₘᵢₙ) substance concentrations.
Table 3. Actual and approved indicators of the water quality source.

| Indicator name | Units measuring | Cmin | Cmax | Source water quality indicators by classes |
|----------------|-----------------|------|------|-------------------------------------------|
|                |                 |      |      | I class | II class | III class |
| Dry residue    | mg/dm³          | 240  | 390  | ≤ 1000  (1500*)                          |
| Sulphates      | mg/dm³          | 53   | 85   | ≤ 500                                    |
| Chlorides      | mg/dm³          | 15   | 35   | ≤ 350                                     |
| Total hardness | mol/m³          | 4    | 5    | ≤ 7 (10 *)                               |
| pH             |                 | 8-10 | 6.5-8.5 | 6.5-8.5 | 6.5-8.5 |
| Color          | degrees         | 20-60| ≤ 35 | ≤ 120 | ≤ 200 |
| Smell          | points          | 2-4  | ≤ 2  | ≤ 3  | ≤ 4  |
| Phytoplankton  | mg/dm³          | 1    | 15   | ≤ 1  | ≤ 5  | ≤ 50  |
|                | cells/cm³       | 10¹-¹⁰⁶ | ≤ 10¹ | ≤ 10³ | ≤ 10³ |
| PO             | mgO/dm³         | 5    | 16   | ≤ 7  | ≤ 15 | ≤ 20  |

Note: * - the norms in agreement with the bodies of the sanitary-epidemiological service.

Currently, the large Volga cities use drinking water lines for drinking water sources of class II for drinking water supply. Water treatment includes: disinfection, coagulation, sedimentation, filtering and chlorination when supplied to the network, which is clearly not enough to bring water to drinking quality.

During the cyanobacteria mass development period, the additional stages of purification from organic and toxic substances are required by applying the membrane technologies, oxidative and sorption methods using ozone and activated carbon.

The main oxidizing agents are chlorine, ozone and chlorine dioxide. These oxidizing agents are commonly used before chemical addition, before filtration, or after filtration as disinfectants. The addition of an oxidizing agent (ozone) in the intake of source water poses two problems with respect to microcystin removal.

The first problem is the need to prevent lysing (destruction) of the cyanobacterial cells. There has already been general agreement that toxin removal is maximized by the intact cells’ removal [12]. The problem remains open of which oxidizing agent can be added at the inlet, which will not lyse cells, but will help oxidize the dissolved extracellular toxins. The chlorination reception is not practiced due to the organochlorine compounds formation and the risk of bacterial cell lysis.

When choosing a production line for water purification, it is necessary first of all to take into account that the removal of micro-cystine from water should be carried out taking into account its location at two levels: extracellular or intracellular.

The intracellular microcystin removal must be carried out without damage to the cyanobacterial cells. Their removal may be carried out using the membrane technologies that allow to filter the cells without mechanical damage.

Two types of membrane filtration are suitable: microfiltration and ultrafiltration, which are commonly used to remove particulate matter from drinking water. Microfiltration and ultrafiltration pore sizes vary from 0,075 to 3,0 μm and from 0,1 to 0,001 μm, respectively. It was found that filtration is very effective in removing intact cyanobacterial cells provided that the water is pretreated, which increases the efficiency of algae cell removal and reduces the membrane contamination.

Removal of extracellular microcystin is achieved by using membrane nanofiltration or adsorption on activated carbon. Activated carbon is obtained in the process of the temperature-controlled processing of carbon-containing material - usually wood, coal, coconut shells or peat.

As a result of such activation, a porous material with a large surface area (500–1500 m²/g) and high efficiency in the organic compounds removal appears. It is usually used in powder (P) or granular (G) form. Activated carbon is used to remove the organic substances that give taste and smell, cyanobacterial toxins, as well as to reduce the total content of organic carbon.
Summary
During the cyanobacteria mass development period on the Kuibyshev reservoir, the water quality deteriorates. In terms of organic matter content, the Volga water does not meet the regulatory requirements for surface sources of drinking water of class I and II. Due to the presence of cyanotoxins in the Volga water, there is a real threat of their ingress into drinking water in excess of the estimated acceptable concentration established by WHO.

An increase in the water temperature of the reservoir under abnormal hydrometeorological conditions leads to an increase in the duration and intensification of the process of mass development of cyanobacteria, which pose an increasing threat to drinking water supply in conditions of global climate warming.

The current ecological state of the Kuibyshev reservoir necessitates the modernization of existing technological schemes for the purification of natural water in the Volga cities in order to reduce the organic substances concentration and prevent toxic pollution of drinking water.

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