Features of the physicochemical water state of reservoirs of energy facilities

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Abstract. In a time when increasing anthropogenic impact on the environment, particularly on the water ecosystems, determine the water status of reservoirs (by physicochemical and biotic indicators) in order to highlight priorities at the field of water protection and management is the urgent question. In this case, the particular significance has lakes located within megalopolis and which is multiple-use objects. The article discusses in detail how to change temperature condition of basin-cooler of heating plant: vertical and horizontal. As a result of analysis of physicochemical indicators the water quality index is displayed. Index allows you to estimate the water quality by the rate of pollution through the use of perspective an integrated indicator—total antioxidant activity. Special attention is given to such physicochemical indicator as redox potential.

Introduction

Thermal power plants (TPP) use a significant volume of water to cool the turbine generators. In accordance with the Rules of technical operation of power plants and networks of Russia, during the operation of technical water supply systems should be ensured uninterrupted supply of cooling water to normative temperature in necessary quantity and the required quality. As a result, formed the overflow heated water. Utilization of secondary energy resources is becoming an urgent problem on thermal power plants. Modern power plants convert 30-40% of fuel heat into useful electrical energy. The rest 60-70% is dispersed into the environment. Temperature of the overflow water at TPP in summer rises to +30-35°C, in winter it is +8-11°C. The temperature potential from +8°C to +35°C is comfortable for almost all biological creatures. At the nuclear power plant the temperature of the overflow water in summer rises to +35-40°C, in the winter it does not drop below +18-20°C [1].

An important aspect of the connection the status of aquatic ecosystems and the energy is the thermal impact on reservoirs of heating plants. The problem becomes particularly acute in cases when lakes are using within the city limits as basin-cooler of combined Heat and Power plant (CHPP).

Water temperature condition of reservoirs of energy facilities

In Kazan (the Tatarstan Republic) the lake Sredniy Kaban is basin-cooler of the Kazan CHPP-1. When choosing the place for power plant the crucial role has played the fact that water in the lake Sredniy Kaban was not only clean, but also soft. In 1866 the famous Russian chemist A.M. Butlerov recommended water of the lake Sredniy Kaban for its high natural qualities for the central urban water supply. As a result of the construction of CHPP-1 and continuing process of water abstraction and discharge, artificial water circulation in the north-western part of the lake is appeared (Figure 1).
After the construction of a dam at the confluence of open offtake in the lake circulation ceased and water masses are moving only due to wind processes. Based on the speed of withdrawal and the volume of water in the lake, it has been calculated that the total water cycle in the lake is going for 96 days. Our researches [2, 3] pointed out that the lake of Sredniy Kaban – lake with artificial thermal regime – belongs to the “very warm” (4074°) according to the number of the heating degree days on the classification of S. P. Kitaev. Modern temperature condition of the lake Sredniy Kaban is characterized by 5 periods [2]: summer stagnation; partial summer and winter, full autumn and spring circulation. When compared to the lake with a natural temperature regime we can see the reduction of one temperature period – fading winter stagnation. During the year the temperature of the water surface layer varies from +0.3°C to +34.5°C and benthic – from +1.9°C to +28.2°C. Significant contributions, especially in winter time, make heated water of Kazan CHPP-1, which does not allow an average temperature drop below +4°C. The large part of the lake (77%) is covered by ice, which lasts 4 months. The temperature of water surface layer in a horizontal direction in the warmest month (July) at the lake of Sredniy Kaban varies within 9°C (from +21°C to +30°C), while at the lake Verhny Kaban (lake with natural temperature regime) –within 2°C (from +26°C to +28°C) (Figure 2).

If at the lake Sredniy Kaban at the place of the heated water influence of CHPP is observed direct stratification in the winter time (Figure 3a), at the lake Verhny Kaban (without thermal pollution) – backward stratification (Figure 3b). At the lake Sredniy Kaban thermocline continues 2 months: July and August (Figure 3c), at the lake Verhny Kaban – 1 month (July) (Figure 3d). At the bottom layer of lakes we can see rising temperature at 0.2-0.3°C associated with the decomposition of organic matter in the subsurface layer of soil.

Thus, thermal anthropogenic impact on the lake is lead to change the temperature condition of the basin-cooler. Coefficient of variation (V%) of water temperature at the lake without thermal pollution is 4.6% and at the lake with thermal pollution is 16.4% on conditions that the air temperature is similar.
Water quality index

For the first time to evaluate the quality of the water has been used new complex index – total antioxidant activity (TAOA). The range of water TAOA at the lake Sredniy Kaban from 2,61 to 6,09 mg.rutin/l [4, 5]. Values of TAOA on the territory of withdrawal of the Kazan CHPP-1 have been higher than on the territory where heated waters inflow to the lake: 4,64 and 3,19 mg.rutin/l respectively. To compare data has done analysis of TAOA of distilled water – 2,61 mg.rutin/l; different brands of drinking water – 3,19 mg.rutin/l; melt water – 3,19 mg.rutin/l; artesian water – 5,37 mg.rutin/l.

In addition to the listed indicators were researched other physicochemical parameters: pH-value, concentration of dissolved oxygen, redox potential (Eh), which entered to the water quality index (IWQ) developed by us. IWQ evaluate the water quality on the degree of contamination through the use of perspective and complex indicator – total antioxidant activity.

This index is obtained from the equation balance between values of antioxidant activity (mg.rutin/l) and abiotic water factors: water surface temperature (°C), dissolved oxygen (mg/l) pH, Eh (mV) (formula 1).
TAOA – total antioxidant activity (mg.rutin/l); Ts – water surface temperature (°С);
Co2 – concentration of dissolved oxygen in the water (mg/l); pH – water pH-value; Eh – redox potential (mV).

Forecast model fidelity confirms by the standard error 0,09 and the coefficient of determination 99,32%.

If the values of IWQ in the range from -1 to +1 it means that water is pure (oligosaprobic in accordance with the data of parallel microbiological analysis). If the values of IWQ in the range from +1 to +2 and from -1 to -2 that is α-mesosaprobic zone. If the values of IWQ in the range from +2 to +3 and from -2 to -3 that is β-mesosaprobic zone. When the values of the coefficient in the range -3 < IWQ < 3 water is contaminated – polisaprobic. Water quality in the area of withdrawal of Kazan CHPP-1 is regarded as the lowest (in the summer period IWQ reaches -3.2 – polisaprobic water quality). The area of heated pollution (confluence of the heated waters of the Kazan CHPP-1 into the lake) is characterized by maximum variability of IWQ (from -2.5 to + 2.4; V = 909.4%). In different periods of time the water quality in this zone is characterized as oligo-, β-mesosaprobic.

Redox potential as a promising monitoring indicator

Eh is a complex physicochemical indicator that is able to indicate water quality [3]. Eh is a measure of the chemical activity of elements or their compounds in reversible chemical processes associated with the change in the charge of ions in solution. Positive values of Eh indicate the oxidizing conditions, negative – on restoration. Eh value is defined by the presence in solution potentially specify ions [6]:

- elements-oxidants, which are capable to accept electrons (Fe3+, Mn4+, S6+, Cr6+);
- elements-reductors, which are capable to give electrons (Fe2+, Mn2+, S).

In addition, the most important oxidant is oxygen, and reductor – organic matter and certain types of bacteria.

Eh researches have their roots in the middle of 20th century (Figure 4). In conditions of active water cycle usually present free oxygen and geochemical environment is oxidative. The Eh value more than 0.15 V, sometimes more than 0.4 V [7].

Figure 4. The results of measurements of pH and Eh values in natural waters by Garrels, 1968 [7].
At a time of slow water cycle oxygen spend on oxidation of organic substances and elements with variable valency (Fe, Mn, As, etc.) and geochemical environment is Gley (oxygen-free). The Eh value usually less than 0.4 V, sometimes less than 0 V (bogs of tundra, taiga and steppe zones, lower horizons of groundwater) [7].

In a very slow water cycle in deep horizons of underground waters is formed reductive atmosphere with hydrogen sulfide, Eh-value < 0, often up to 0.5 V due to extremely weak inflow of oxygen and active work of sulfate-reducing bacteria [6].

Interest to Eh researches doesn’t extinguished in the XXI century. Research of physicochemical indicators of rivers in the Republic of Tatarstan has shown that the range of variation of Eh from -21,1 mV to -166,1 mV [60]. The amplitude of variational series is 145 mV. Focusing on major rivers, the territory of the Tatar ASSR divided into 3 parts on the orography – Predvolzhie, Predkamie and Zakamie. Predkamie on the river Vyatka is divided into West and East. Zakamie on the rivers Verhnii Chereshman and Sheshma River is divided into Western Zakamie (low) and Eastern Zakamie (high). In accordance with this division all collected data of Eh-value in rivers are shown in Figure 5.

![Figure 5](image URL)

Figure 5. The mean values of Eh (mV) with the standard error of average in Kuibyshev reservoir and the rivers of the Republic of Tatarstan.

From data represented in Figure 5 shows that the minimum variations is in the Kuibyshev reservoir and on the Kama river. Water sampling in the Kuibyshev reservoir was in 3 locations around Kazan (next to the urban-type settlement Vasilevo, Oktyabrskoe rural settlement and in the Kirovskyi district of Kazan) and 2 locations near the Tolyatti city (in Primorskii district of Tolyatti and near of Fedorovskie luga of Tolyatti). The value of Eh in Kuibyshev reservoir increased from the urban-type settlement Vasilevo to Fedorovskie luga of Tolyatti (from -78.5 mV to -63 mV).

Maximum variation of Eh values and maximum the standard error of average observed in the rivers of Western Predkamie (Eh values range from -21,1 mV to -166,1 mV) and Predvolzhie (Eh values range from -38,8 mV to -104,7 mV).

In general, the range of Eh values changes in lakes and natural ponds more wide compared to Eh values in rivers. For example, only in the Republic of Tatarstan the range of Eh values changes in lakes from 7,5 mV to -226,4 mV. The amplitude of variational series is 233,9 mV. It is in 1.6 times higher the Eh amplitude in rivers. Our researches corroborate direct dependence of Eh from pH [8], therefore the range of Eh values conforms to the values of pH from 5.87 to 9.85. For reservoirs,
experiencing the action of energy facilities (for example, the Sredniy Kaban lake of Kazan) the average value of Eh in zone, not suffering from action of energy facility (Kazan CHPP-1), is -53±8,5 mV. In the area of direct impact of energy facility Eh value drops to -80 mV, average value is -70±8,5 mV [2]. Thus, Eh is more sensitive indicator to determine changes of physicochemical condition of the water compared to pH.

One of the most effective ways of recycling low-potential overflow water is creating energobiological complexes.

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