Prospects of test systems use for assessing the water quality of small rivers and reservoirs in the Samara region

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Abstract. Protection against pollution of surface and ground waters is implemented at different levels of state environmental protection management, including the regional one. There are a number of programs in Samara region aimed at providing residents of the region with high-quality drinking water and environmental rehabilitation of water bodies, including small rivers. Information support for making management decisions in this area is the data of environmental monitoring. On the example of the data on dissolved oxygen content in the water of rivers and reservoirs of Samara region, the shortcomings of the existing system of environmental monitoring were identified, which covers only a small part of water bodies of economic importance. At the model object, which was chosen as one of the ponds of Samara, the capabilities of the test systems for measuring the content of dissolved oxygen were shown. It was also shown the desirability of using the test systems for water bodies in remote areas of the region as part of the expansion and improvement of the existing environmental monitoring system.

1. Introduction

Article 42 of the Constitution of Russian Federation enshrines the right of every citizen of our country to a favorable environment, which includes the effective and rational use of all types of natural resources, including water. The assurance of quality drinking water is one of the vital interests of the individual, which are under the protection of the state. Over the past years on the territory of the Samara region different programs have been implemented that allow concentrating and using resources to achieve results in specific areas, such as preventing further pollution of water bodies by gradually eliminating existing sources of pollution and preventing the emergence of the new ones, ensuring the rational use of water, primarily for drinking and household needs of the population, finding the ways to replenish fresh water supplies and their rational distribution. Since the surface water bodies are the main sources (60% of the total water intake for drinking purposes) for population provision of drinking water, the water quality of the surface bodies is of particular importance. One of the priority directions of the environmental policy on the territory of Samara region is the improvement of sanitary and ecological situation at surface water bodies.

In 2004 the region approved the program “Assurance of the population of Samara region with drinking water for 2005–2010”. The regional target program "Development of the water management complex of Samara region in 2013-2020" was adopted in 2012. The priority direction of the above-mentioned programs was the provision of the population with high-quality drinking water that meets the...
safety and harmlessness requirements established by the sanitary and epidemiological rules. Currently, in order to improve the quality of drinking water supply for the population in the Samara region, the Ministry of Energy, Housing and Public Utilities of Samara region is taking part in the implementation of the federal project "Clean Water" of the national project "Ecology”, approved by the Decree of the President of Russian Federation dated 07.05.2018 No. 204. One of the priority directions of the environmental policy on the territory of Samara region is the improvement of sanitary and ecological situation at surface water bodies [1].

On the territory of Samara region small reservoirs have been created for economic needs in addition to the large Kuibyshev and Saratov water storage basins. The region has 11 reservoirs on the local runoff with a capacity of 4 to 112 million m³ with a water surface area of about 1840 km² [2]. Also there are more than 500 ponds on small rivers in the Samara region. Reservoirs and ponds are used for irrigation, fish farming, water intake, fire-fighting water supply in the arid administrative districts of the region. Water quality in small reservoirs and ponds is formed under the influence of natural factors of pollution and anthropogenic load on water bodies. Pollution enters the water bodies mainly with wastewater discharged from sewage treatment plants of settlements, agricultural farms, industrial enterprises and services, with snow melt water from the agricultural lands, rain washings from the soil, brought by the small rivers. According to long-term observations, the level of water pollution in small reservoirs and ponds of Samara region remains high and does not meet sanitary requirements on chemical and biological oxygen consumption, the content of suspended solids, phenols, and iron. In a number of ponds and reservoirs, especially in large cities of the region, there is an excess of iron (up to 5 MPC) and phenol (up to 1.6 MPC) in water [3]. The average annual concentration of difficult-to-oxidize organic substances (COD) in different periods is from 2.0 MPC to 3.2 MPC. The average annual content of easily oxidized organic compounds (according to BOD5) is annually noted at the level of 2.0 to 3.0 MPC.

One of the most important factors ensuring the ecological state of water bodies is the amount of oxygen dissolved in the water, which determines the activity of self-cleaning processes, determines the value of redox potential and, to a large extent, the direction and rate of the processes of chemical and biochemical oxidation of organic and inorganic compounds. Constant monitoring of the oxygen regime is an urgent task, since the determination of oxygen in surface waters is necessary for assessing the quality of surface waters and regulating the wastewater treatment process in current conditions.

The aim of the present work is to assess the prospects of using the test systems in the framework of water bodies environmental monitoring on example of determining of dissolved oxygen content.

2. Materials and methods

A small reservoir within the boundaries of Samara - the pond named Krugly (situated opposite the «Pyramida» shopping center), was chosen as a model system for studying the features of use of laboratory and test methods for the determination of dissolved oxygen in the water. Pond diameter is about 60 m, mirror area - 3151 m², shallow water area (less than 2.0 m) - 2069 m², average depth is about 1.5 m, maximum - 3.12 m [4], alimentation - both from rainfall and groundwater.

To measure the content of dissolved oxygen, composite samples were used; the work was carried out during the summer low-water period (July). Water samples were taken according to the standard method [5], oxygen was determined on the day of sampling. The content of dissolved oxygen in water was carried out in parallel by two methods - iodometric titration and using a test system based on a modified Winkler reaction.

Today, iodometric determination of dissolved oxygen in water is the basis for at least two existing methods (its metrological characteristics are given in table 1).
Table 1. Measurement uncertainty characteristics by iodometric method

| Index                                      | PND F 14.1:2:3.101-97 | RD 52.24.419-2019 |
|--------------------------------------------|------------------------|-------------------|
| Measurement range of dissolved oxygen mass concentration, mg / l | From 1.0 to 15.0 inclusive | From 1.0 to 15.0 inclusive |
| Reiteration index (relative standard deviation of reiteration),% | 5                      | 1-3               |
| Accuracy index (limits of relative error at probability $P = 0.95$),% | 16                     | 3-10              |

For both methods (table 1), the measurement range is from 1 to 15 mg/l of dissolved oxygen, but the limits of the relative error differ significantly. In this work the technique [6] was implemented.

Visual colorimetric test system (VISOCOLOR®ECO Oxygen (MACHEREY NAGEL GmbH & Co. KG), gradation 0 – 1 - 2 - 3 - 4, 6 - 8 - 10 mg/L $O_2$) was used to measure the oxygen content directly at the sampling site.

3. Results and discussion

The oxygen content, determined by the method [6], amounted to 0.5 mg/l, should indicate on the phenomenon of fish kill in the pond. Meanwhile, by visual inspection of water area and the coastline, such signs as massive water bloom, a decrease of its transparency, the death of aquatic organisms were not established. Oxygen determination performed at the sampling site using a test system established a concentration of 4 mg/l, which is lower than the normative one, but exceeds the result obtained according to [6] by eight times. Desorption of dissolved oxygen was facilitated by the high air temperature on the day of the work (up to 35 °C), as well as the time required to deliver the sample to the laboratory.

The results obtained on the model system (a pond within the city of Samara) were further used by us to assess the effectiveness of the existing approach to the determination of dissolved oxygen in the water of rivers and reservoirs of Samara region and to develop proposals for its development. The hydrographic network of Samara region is represented by Volga River and its tributaries. Within the region, the river is represented by Kuibyshev and Saratov water storage basins, with a surface area of 191 thousand hectares, the length of Volga river within Samara region is 364 km. There are more than 220 rivers and small streams with a total length of more than 6.5 thousand km, more than 1000 reservoirs and ponds.

Volga Interregional Territorial Administration of the Federal Service of Hydrometeorology and Environmental Monitoring (FSHandEM) on the territory of the Samara Region carries out stationary observations of water quality of Kuibyshev, Saratov and Vetyanskoe reservoirs, 12 largest rivers according to 56 indicators. It is quite obvious that the scope of the work being carried out does not correspond to the scale of the task. Moreover, the lack of data on the level of pollution of small rivers that have a hydrographic connection with those water bodies where observations are already being carried out, limits the possibilities of interpreting the results for medium and large rivers.

There are no observational stations on the water bodies in a number of southern districts of the region (Bolsheglushitsky, Bolshechernigovsky, Alekseevsky, Pestravsky, Krasnoarmeisky), i.e. monitoring activities are not carried out not only on small rivers, including intermittent ones, but also on reservoirs - Polyakovskiy, Mikhailo-Ovysansky and a number of others. This is of great concern due to the fact that the ongoing regional programs on ecological rehabilitation of water bodies and the assurance of the population of the region with high-quality drinking water, in fact, are adopted in conditions of uncertainty, in the absence of complete and reliable information on the actual state of water resources.

For Samara region, especially its southern districts, to this day dug ponds remain the most important source of water supply (figure 1).
Figure 1. Pond fish culture of Middle Volga [7].

Its importance for households and private subsidiary farming is undeniable. For our region dug ponds have traditionally been a source of uninterrupted water supply, since they accumulate snowmelt runoff, which accounts for up to 70% of the yearly rainfall rate in Samara region.

Vast majority of water bodies in Samara region are characterized by the multiple use of water resources in at least two or three areas - for example, household and drinking water supply, fish farming and recreation. It should be emphasized that the content of dissolved oxygen as the most important indicator of water quality [8] and the trophic status of a water body [9] is fixed for a number of types of water use: for example, fishery [10] and recreational [11]. Thus, the organization of flexible and mobile monitoring is not only a matter of obtaining information about the state of a component of natural environment, but also of a social issue. When developing proposals for monitoring the content of dissolved oxygen, it is necessary to take into account a number of features: its expected concentration (based on the long-term observations of the other water bodies of Samara region), as well as the severity of factors that contribute to oxygen desorption from the selected water sample and distortion of the analysis results.

The expected oxygen concentration was estimated by us (figure 2) according to the FSHandEM data published in [12-16] for the period from 2011 to 2015. Monitoring objects are twelve small rivers of Samara region and three reservoirs (Saratov, Kuibyshev and Vetlyanskoe).

Figure 2. Distribution of the average annual content of dissolved oxygen, mg / l, in water bodies of Samara region (compiled according to [12-16]).
The analysis of the open sources data shows [12-16] that in recent years the content of the dissolved oxygen was 6-8 mg/l in 52% of cases, 4-6 mg/l - in 26% and 8-10 mg/l - 12% cases. It should be noted that low concentrations, from 0 to 4 mg / l, were also recorded, while no values above 10 mg/l were observed. Thus, when choosing a method for determining oxygen, the measurement range can be significantly narrowed relative to the standard one [6].

The content of dissolved oxygen in water is determined by a number of factors, both related to the entry of pollutants into the water body from the outside, and of a purely natural character, including those related to the characteristics of the water body itself. We used Vetlyanskoe water storage basin as a model system for small rivers and storage lakes in the southern regions of Samara region. It was created on the basis of Vetlyanka river, a tributary of the river S’ezzhaya, which flows into Samara river, and a pond near the village of Verhnes’ezzhée (table 2).

**Table 2.** Information about some water bodies of Neftegorsk district of Samara region [7,17]

| Water body                                | Inflow place       | Reservoir basin area, thou. sq. km | Length, km | Depth (maximum), m | Flow rate, m/s |
|-------------------------------------------|--------------------|------------------------------------|------------|-------------------|----------------|
| Vetlyanka                                 | S’ezzhaya          | 0.13                               | 50         | -*                | -*             |
| S’ezzhaya                                 | Samara             | 2.41                               | 108        | 1.5               | 0.01-0.36      |
| Samara                                    | Volga              | 46.1                               | 575        | 2.0               | 1.5            |
| Bol’shi pond (Verhnes’ezzhée village)    | Drainless water body | -*                           | 1.6        | 3                 | 0              |
| Vetlyanskoe water storage basin           | Drainless water body | 0.45                             | 13.7       | 12                | 0              |

* - no data available

Those water bodies, on which environmental monitoring is not currently carried out, are similar in its characteristics both Vetlyanka river and Bolshoi pond: low flow rates, small volume or flow rate of water, shallow depths, which creates unfavorable conditions for oxygen dissolution especially at high temperatures. In addition, the reservoirs of southern districts of the region (in particular, Vetlyanskoe water storage basin) have a high level of water salinity - up to 3000 mg/l and more, which also reduces the solubility of oxygen. Thus, for small rivers, streams, and ponds of the Samara Region, the expected values of dissolved oxygen concentrations are low. Thus, for small rivers, streams, and pools of Samara region the expected values of dissolved oxygen concentrations are low. All this forces us to pay attention to the test systems, which, although often lose to the laboratory methods in the magnitude of the measurement range, but allow avoiding sample transportation, which, as our results showed, will also lead to an underestimation of the oxygen content in the sample. Moreover, the regulatory document [5] establishing the rules for the collection and storage of water samples for the case of dissolved oxygen determination provides for two equivalent options of the recommended location for determining the indicator: "laboratory" and "at the sampling site".

**4. Conclusion**

The results of the environmental monitoring are the basis from which the goals, objectives and environmental policy of the whole region are formed. Within the framework of the present work, it was revealed that medium-term planning of environmental measures is impossible without full-scale studies of the oxygen regime of economically important water bodies. Our practical assessments of the characteristics of test systems have shown that the acuteness of the problem of obtaining timely information on the quality of water in pools and reservoirs in the southern regions of Samara region can be at least partially removed by using the appropriate test systems.
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