Features of chemical composition of small river Khodtsa

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Abstract. The article presents the heavy metals and metalloids concentration in the small river Khodtsa. They testify the excess of MPC along the entire river bed in all periods and years of studies on iron; in the lower flows – on cadmium, as well as the content of manganese and nickel close to the MPC. During the observation period, a tendency for a decrease in the COD values from the upper flow to the lower one was noted. In the upper flow, the CODs were 1.7 and 2.5 times higher compared to the middle and upper flows, and the BOD was 1.6 and 2.3 times, respectively. Based on combinatorial index, the extreme level of water pollution was determined.

1. Introduction

Many small rivers are reserves of clean drinking water, whose supply is now steadily declining. The vulnerability of small rivers due to their size and low ability to withstand anthropogenic impact leads to qualitative and quantitative changes in water bodies, i.e. to the emergence of environmental problems. This enables to consider small rivers as an indicator of the ecological state of not only water-collecting areas but also water bodies in general [1, 2]. Flowing directly into large water bodies, they are able to transform their composition and quality, at least in local areas at the places of outfall (channel) [3, 4]. In modern conditions of intensive nature management, anthropogenic impact on river ecosystems often becomes the determining factor in the transformation of the component composition of the aquatic environment. Amid such natural factors dominating in the formation of the chemical composition of waters as the composition of soils with which the waters come in contact and the composition of rocks underlying the soil, the anthropogenic factor often becomes decisive [5].

2. Problem Statement

Khodtsa River, which belongs to the Oka Basin District and originates in the vicinity of the town of Elektrostal, Moscow Region, belongs to the category “small rivers”. The volume of wastewater annually entering the river from the enterprises of Elektrostal is over 4,146 thousand m³. At the same time, only 11% of their releases are provided with treatment facilities, which indicates the insufficient capacity of the city’s treatment facilities. The main pollutants can also get into the Khodtsa River with storm water (Pb, Cd) and sewerage (Cd) flows, and as a result of atmospheric emissions.

In this regard, the purpose of our research was to study the intra-annual variability of the chemical composition of the water of the Khodtsa River during the spring flood, summer and winter low-water periods.
3. Materials and methods
Water from the river was sampled in accordance with the requirements of State Standard 31861-2012 “Water. General requirements for sampling”. The variability of the chemical composition of the Khodtsa water for the period 2018–2020 is considered according to such indicators as the content of basic cations and anions, iron (total), heavy metals: cadmium, lead, copper, zinc, nickel, manganese, and substances resistant to oxidation (according to BOD and COD). The long-term dynamics of water quality and the degree of its pollution was assessed based on a combination of differentiated and complex assessment methods. A comprehensive assessment enables to judge the hydrochemical state of the aquatic environment by water quality indicators and classify the degree of its pollution under anthropogenic load. The most informative complex indicators of water quality include the specific combinoratorial index of water pollution and the class of water quality. The value of the specific combinoratorial index varies depending on the degree of water pollution from 1 to 16. The higher value of the index corresponds to the worse water quality [6]. When assessing a complex indicator, the optimal number of ingredients taken into account is from 10 to 25. Therefore, this method enables to assess and classify water pollution by a wide range of ingredients and indicators of its quality. Usually, the MPC of harmful substances for water bodies of fishery, drinking or cultural and domestic water use is applied as a standard, i.e., the methodological basis of an integrated method is an assessment of the degree of water pollution based on the totality of pollutants. The basis of the differentiated method is the assessment of the water quality of water bodies for individual pollutants using their MPC and statistical methods. The water quality classified with regard to the values of the specific combinatorial index of water pollution, enables to divide surface waters into 5 classes depending on the degree of their pollution: 1st class denotes conditionally clean water; 2nd class – slightly polluted; 3rd class – contaminated; 4th class – dirty; 5th class – extremely dirty [6].

4. Results and Discussion
Natural waters are classified according to a number of characteristics, the simplest of which is the salinity or mineralization of water. Mineralization of water shows the total content of all minerals present in it. The change in the hydrological phases and water content of the watercourse causes changes in the mineralization and chemical composition of the waters. Thus, the total content of all mineral substances found in the chemical analysis of water during the flood in the river source was 87.9, in the autumn low-water period – 140.5; in the middle water flow – 133.8 and 195.5; in the lower water flow – 120.6 and 202.2 mg/kg, respectively. Thus, the water can be categorized in the following way: with very low salinity (less than 100 mg/dm³), low salinity (100–200) and medium salinity (200–500). Since the Khodtsa, like other small rivers, is a receiver of household, industrial and agricultural wastewater having high concentrations of harmful substances, the analysis of the hydrochemical composition of water in space is of great interest. The nitrate content at the Khodtsa source was 1.5–1.7 mg/dm³ (April-November). Downstream, the level of the toxicant increased by more than 2.5 times. In the channel, they are diluted, which leads to a decrease in concentration at the mouth. The amount of nitrites along the entire length of the watercourse is below the permissible concentrations (0.05–0.14 mg/dm³). No spatiotemporal changes in their concentration were revealed. Phosphates were also within reasonable bounds. As they approached the river mouth, their concentration increased. At the mouth, in comparison with the source, the amount of phosphates in April-November increased more than 6 times. The content of sulfate ions was low. At the same time, their concentration increased by the fall by 1.3–2 times. Chlorides having the highest migration capacity of all anions, are one of the criteria for surface water pollution. In the Khodtsa River, the concentration of chlorides increases from source to mouth. It is necessary to note the higher content of chlorides in the middle course of the river at all periods of determination. At all points of water sampling, the concentration of HCO₃⁻ in autumn exceeds their concentration in spring during the flood period. Probably, the intense melting of snow being soft water contributes to the dilution of natural waters and, in general, to a decrease in hardness. The fluorine concentration varied in space and time from 0.24 to 0.33 mg/dm³, which is significantly lower than the MPC (1.5 mg/dm³).
The conditions of individual years leave an imprint on the space-time concentrations of individual compounds. Thus, the absence of precipitation almost until the summer low water period in 2018 reduced the river flow in the upper flow, which led to a sharp increase in the content of ammonium ions in the water source (more than 20 times in the middle flows and more than 50 times in the lower flows) and iron (more than 6 times in the middle flows and more than 11 – in the lower flows) (Table 1). It should be noted that the content of the ammonium cation in the upper flows exceeded the MPC by 9 times, and the iron content exceeded the MPC in the upper flows by 61, in the middle flows by 10, and in the lower flows by more than 5 times. Also, the content of oil products decreased from source to mouth in August.

### Table 1. Indicators of water quality in 2018

| Determined indicator          | Upper flow 02.08.2018 | Middle flow 02.08.2018 | Lower flow 02.08.2018 |
|-------------------------------|------------------------|------------------------|------------------------|
| pH, pcs.pH                    | 7,68±0,20              | 7,42±0,20              | 7,74±0,020             |
| Ammonium ion (nitrogen), mg/dm³| 18,7±3,7               | 0,90±0,18              | 0,37±0,08              |
| BOD full, mg O₂/dm³           | 12,7±1,3               | 8,0±0,8                | 5,5±0,6                |
| COD, mg O₂/dm³                | 14,1±2,8               | 8,4±2,5                | 5,7±1,7                |
| Oil products, mg/dm³          | 0,084±0,029            | 0,076±0,027            | 0,011±0,004            |
| Aluminum, mg/dm³              | <0,04                  | <0,04                  | 0,2±0,01               |
| Iron, mg/dm³                  | 18,2±1,8               | 3,0±0,4                | 1,58±0,24              |
| Arsenic                       | 0,002±0,0012           | 0,002                  | 0,0034±0,0015          |
| Mercury, mg/dm³               | <0,0001                | <0,0001                | <0,0001                |

Analysis of water bodies refers to trace analysis. Due to the large number of standardized indicators, it is almost impossible to give a reliable assessment of water quality using only information on the content of individual components in it. The water quality assessment system should be based on the so-called generalized indicators being quantitative characteristics of water properties determined by direct measurement, conditioned by the joint effect of the components found in them and necessary for assessing its quality, primarily COD (chemical oxygen demand). During the observation period, there was a tendency for the COD values to decrease from the upper to the lower flows. Thus, in the upper flows, the COD was 1.7 and 2.5 times higher than in the middle and upper flows; TBOD — 1.6 and 2.3 times, respectively. In our opinion, this is due, first of all, to the discharging a large amount of pollutants (oil products, soot, various kinds of organic waste, etc.) accumulated during the winter period, melt and rainwater into the river. It is also possible that humic substances and other decay products of plant and animal organisms can be washed out of the soil. An increase in oxidizability, as a rule, is a consequence of wastewater discharge [7, 8].

The use of two different indicators being oxygen consumption by biochemical and chemical processes is not accidental. The ratio of BOD and COD enables to determine the nature of water pollution and select an effective treatment method. The COD value is usually greater than the BOD. A small difference between these indicators denotes that biological purification methods will lead to a good result, and vice versa, a large gap in the COD value indicates that chemical purification is the most effective. The water in the Khodtsa river is characterized by very low biochemical parameters (TBOD /COD). For the top point, it is 0.90; middle and bottom points – 1.05 and 0.96, respectively. In 2018–2020 there was no COD value not exceeding the standard recorded. This state of the river basin cannot be explained only by polluting the water by melt water.

The level of the river toxic pollution in terms of the content of inorganic substances (heavy metals and metalloids) established in the autumn-winter low-water period, indicates an excess of the MPC along the entire river bed in all periods and years of research on iron, in the lower flows – on cadmium, as well as close to MPC content for manganese and nickel (table 2).

During the summer low-water period in the upper flows of the river, in some years the MPCs for cadmium were exceeded by 10 times, and for lead – by 2 times.
Table 2. Content of inorganic toxicants in the Khodtsa River water, average for 2018–2020

| Determined indicator | Upper flow | Middle flow | Lower flow |
|----------------------|------------|-------------|------------|
| Iron                 | 30.5±5.3   | 5.9±0.6     | 12.9±2.3   |
| Arsenic              | 0.009±0.004| 0.007±0.003 | 0.005      |
| Manganese            | <0.01      | <0.01       | 0.077±0.019|
| Nickel               | 0.015±0.003| 0.01        | 0.015±0.003|
| Copper               | <0.01      | <0.01       | 0.025±0.008|
| Zinc                 | 0.011±0.003| 0.012±0.004 | 0.046±0.013|
| Strontium            | <0.25      | <0.25       | <0.25      |
| Cadmium              | <0.0005    | <0.0005     | 0.01±0.003 |
| Lead                 | <0.005     | <0.005      | 0.0052±0.001|

The quality of water in the whole Khodtsa basin varies from class 4 “dirty” to class 5 “extremely dirty”. No abrupt changes in the dynamics of river water quality indicators were found during the study period.

5. Conclusion

The assessment of the water quality of the Khodtsa River in terms of hydrochemical indicators determines the priority measures aimed to increase its ecological reliability: eliminating unorganized discharge of surface runoff; cleaning and improving coastal areas of populated areas; equipping enterprises of the agro-industrial complex with waterproof manure storages, slurry collectors; improving the objects of individual housing and summer cottage construction. To improve the quality of water in a reservoir, it is advisable to use methods of activating self-purification processes, as well as to purify it using bioengineering technologies [9, 10].

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