Role of anthropogenic factor in formation of hydrochemical state of the Tobol river

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Abstract. The hydrochemical indicators of water quality in the Tobol River within the Tyumen Region have been determined. The priority pollutants are assessed. The study established an increased content of organic substances (BOD₅) and ammonium nitrogen; high concentration of nitrites, iron, copper, zinc, phenols and petroleum products. Saturation with oxygen is 50-60%. The maximum values of zinc are fixed in section c. Korkino 10.8 times the MPC; in the areas of Yalutorovsk (above the reset level) and Yalutorovsk (below the reset level) nitrites 26.4 - 18.8 MPC, copper 8 - 9.5 MPC, oil products 26.8-20.6 MPC respectively; in the city of Tobolsk - ammonium nitrogen - 3.03 MPC, iron - 17.3 MPC; The number of phenols did not have pronounced gradations and was distributed relatively evenly in all sections - 7-10 MPC. The index of water pollution is calculated, according to which the quality of water in different sections of the river corresponds to the class from "polluted" to "extremely dirty".

1. Introduction

The main factors of economic activity, which affect the hydrochemical parameters of resources, are municipal and industrial water consumption, irrigation and watering of lands, seasonal and long-term regulation of the flow of reservoirs, agrotechnical measures [1,2].

The main problems affecting the water quality in the Tobol River are:
1. Pollution of surface waters due to transit transfer of pollutants from overlying territories;
2. Lack of water for drinking and domestic water supply in low-water years;
3. The impact of water management systems on the state of water bodies;
4. The influence of the anthropogenic factor on the size and regime of the flow of water bodies due to regulation of the flow of reservoirs, the influence of water intakes and wastewater discharges.
5. Emergency situations at hydraulic structures, as well as treatment facilities or a violation of their use;
6. Failure to comply with the established regime for the use of water protection zones of water bodies and their coastal strips;
7. Discharge of untreated sewage into rivers through concentrated sources of pollution;
8. Non-normative work of sewage treatment plants;
9. Use of the water area for the purpose of conducting various activities: the placement of underwater pipeline crossings, dredging, sand mining by a hydromechanical method [3].
The aim of this work is to assess the water quality of the Tobol River within the Tyumen Region in terms of hydrochemical indicators, to establish the level of contamination with biogens, heavy metals, oil products, phenols and synthetic surface-active substances.

The Tobol River is the most abundant and the second largest tributary of the Irtysh (after the Ishim River) flows into Tobolsk. It originates in the Kustanai region (Kazakhstan), on the border with the Chelyabinsk region, crosses from the south to the north the Kurgan region and five districts of the south of the Tyumen region (Uporovski, Zavodoukovsky, Yalutorovsky, Yarkovsky and Tobolsk). The length of Tobol is 1591 km, including within the Tyumen region - 570 km, the basin area is 426 thousand km² [4].

The water is weakly alkaline throughout the year: the average pH value of the pH decreases from 7.6 in the Uporovskoye, Zavodoukovskii and Yalutorovskiy region to 7.3 in the Yarkovsky region and up to 7.0 in the Tobolsk region.

The river is transitory, polluting substances come not only from the factories located in the territory of the Tyumen region, but also from adjacent ones, including from Kazakhstan.

The sources of pollution of the rivers of the Irtysh basin by organic substances, biogens, pesticides (including heavy metals) and other pollutants are agricultural enterprises (agriculture, livestock). Polluted waters fall with organized, unorganized (area) runoff, including from urban areas

2. Subjects and Methods
Samples were selected on five sites:
- The stitch №1 - r. Tobol in the village of Korkino (transboundary border: the border of the Tyumen and Kurgan regions);
- Stvor №2 - r. Tobol above the city of Yalutorovsk at 2km (further Yalutorovsk VIZ);
- Stem №3 - r. Tobol below the city of Yalutorovsk at 2.5km (further Yalutorovsk NIZ);
- Strok №4 - r. Tobol in the village of Ievlevo;
- Stvor №5 - r. Tobol in the city of Tobolsk.

Sampling was carried out by standard methods in accordance with GOST 51592- 2000 “Water. General requirements for sampling” [5].

The chemical analysis of the water was carried out according to certified methods [6-14]. BOD₅ was measured with a small-sized “MARK-201” on a dissolved oxygen analyzer.

The water quality in the Tobol River was assessed on the basis of a system of indicators in accordance with the generally accepted standards of MPC of harmful substances for the water of fishery water bodies. The degree of pollution was determined on the basis of the "Integrated Environmental Classification of the Quality of Surface Waters of the Land by O Oksiuk and V Zhukinsky "[15,16].

3. Results and discussions
In surface waters, the dissolved oxygen content can be in the range from 0 to 15 mg/dm³, it is subject to seasonal and diurnal changes, its deficiency can be observed in eutrophied and heavily polluted water bodies, as well as at the end of the long ice period. Reducing the concentration to 2 mg/dm³ causes a mass death of fish and other hydrobionts [17].

The results of the studies did not reveal the threshold values of dissolved oxygen in water (Figure1), the concentration of which was within the normal range and had values of 7.01-9.18 mg/l, although it did not reach 100% saturation. The amount of easily oxidizable organic substances (according to BOD₅) characterizing the activity of the saprophytic microflora consuming oxygen in the decomposition of easily oxidizable organic matter was above the MPC in all directions 1.5-2.1 times (Figure 2), only in the Tobolsk area the BOD₅ index was 1.22 mg/l has not reached the norm. The value of BOD₅ decreased downstream from the line village Korkino to the alignment of Tobolsk.
The analysis of the data (Figure 3) showed the following: content of ammonium nitrogen exceeded the MPC 1.3-3.03 times in all investigated sections. The highest values were recorded in areas of Yalutorovsk: 1.142 mg/l (VIZ) - 1.017 mg/l (NIZ) and in Tobolsk - 1.212 mg/l. The concentration of nitrites (Figure 4) was high in Korkino - 10.6 times the maximum permissible concentration; Yalutorovsk (VIZ) - 26.4 MAC; Yalutorovsk (NIZ) - 18.8 MPC and elevated in the range of the village Ievlevo - 2.8 MPC. In the alignment of Tobolsk, its values were at the level of the standard.
Reduced oxygen saturation (50-60%), increased nitrogen content of ammonium, and especially nitrite, indicates saprobic contamination of anthropogenic origin. Thus, the smallest content of oxygen and a high concentration of nitrogen nitrite was observed in the most polluted areas with organic matter. Korkino - Yalutorovsk (VIZ) - Yalutorovsk (NIZ): 7.01 - 8.03 - 7.75 mg/l oxygen and 0.213 - 0.529 -0.377 mg/l of nitrates, respectively.

The content of nitrates (Figure 5) was insignificant in all sections and was practically on the same level from 0.34 to 0.52 mg/l with a maximum permissible concentration of 9.1 mg/l. The concentration of iron (Figure 6) was high in all sections and amounted to 6.2-17.3 MPC. The maximum content is typical for sites with. Korkino - 1,44 mg/l, the city of Yalutorovsk (NIZ) - 1,17 mg/l and the city of Tobolsk - 1,73 mg/l. Such a high concentration of the element, even higher than that of the basin of the Ob-Irtysh basin (0.3-0.5 mg/l), may indicate its anthropogenic origin.

The content of copper (Figure 7) in the water of the river turned in the range of 4.31-9.55 mcg/l at a value of MPC for fishery water reservoirs of 1 mcg/l. The highest concentration was recorded in the alignment of the city of Yalutorovsk (NIZ) - 9.5 MPC. The concentration of zinc (Figure 8) is determined above the MAC level in all the analyzed areas. Exceedance of MPC was from 1.7 to 10.8 times.

Copper and zinc are elements of a double genesis. They are vital for all living organisms in certain concentrations, including in the composition of enzymes or their activators, which catalyze all biochemical processes, the fulfillment of the most important biological functions in the processes of
photosynthesis, respiration, and oxidation-reduction reactions. However, elevated concentrations are toxic to aquatic organisms [18].

The number of phenols (Figure 9) did not have any significant differences in all the study sites, exceeding the MPC was 7-10 times, with a maximum content of 0.01 mg/l in the city of Yalutorovsk (NIZ). Oil products come to water objects in various ways: with wastewater from oil refineries, oil, chemical, metallurgical and other industries, when oil is transported by water, as a result of intensive navigation, with domestic wastewater. During the observation period, the content of petroleum products (Fig. 10) in the water of the Tobol River ranged from 0.13 to 1.34 mg/l.

Synthetic surfactants (Figure 11) were present in small amounts, their values were below the MPC level and were from 0.02 to 0.05 mg/l.

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**Figure 8. Zinc Content in Water of the River Tobol, mcg/l.**

**Figure 9. Content of Phenols in Water of the River Tobol, mg/l.**

**Figure 10. Content of Oil products in Water of the River Tobol, mg/l.**

**Figure 11. Content of Surfactants in Water of the River Tobol, mg/l.**
The hydrochemical indices of water had the following values: by the content of dissolved oxygen, BOD$_5$, ammonium nitrogen, nitrites, iron and phenols, water in the r. Tobol, entering the territory of the Tyumen region, in alignment with Korkino can be classified as "polluted"; zinc and petroleum products recorded a high content - water "dirty", for copper and synthetic surfactants - "satisfactory cleanliness", for nitrates - "clean". As we approach Yalutorovsk (VIZ), the degree of water pollution increases with an ammonium ion - to "heavily polluted", nitrites - to "extremely dirty", copper - to "moderately dirty". The content of oil products in the alignment of the city of Yalutorovsk (VIZ) is increased by 4 times in comparison with the section Korkino - water is also characterized as "extremely dirty". The tendency of the lowered content of dissolved substances in the section c is traced. Ievlevo: according to BOD$_5$, ammonium ion, nitrites, zinc and petroleum products. The main pollutants on the site of Tobolsk remain ammonium nitrogen, common iron, copper, zinc, phenols and petroleum products.

We have determined the index of water pollution (IWR) [19, 20]. As a basis for the calculation of IWR six indicators are taken: the concentration of dissolved oxygen and the value of BOD$_5$, nitrogen nitrite, total iron, zinc, oil products. Thus, the value of the water pollution index was as follows: Korkino - 7.7 units, which corresponds to the 6th grade "very dirty"; Yalutorovsk (VIZ) - 12 units, which corresponds to the 7th grade "extremely dirty"; Yalutorovsk (NIZ) - 10.6 units, which corresponds to the 7th grade "extremely dirty"; with the. Ievlevo - 3.32 units, which corresponds to the 4th class "polluted"; The target of the city of Tobolsk is 6.46 units, which corresponds to the 6th grade "very dirty".

4. Conclusion
Thus, the dynamics of the average hydrochemical indicators of water in the Tobol River within the territory of the Tyumen Region indicate that the priority pollutants are organic substances (BOD$_5$), ammonium nitrogen, nitrites, common iron, heavy metals (copper and zinc), petroleum products and phenols. The greatest amount of pollutants is noted in the sections Korkino, Yalutorovsk (VIZ), Yalutorovsk (NIZ), the city of Tobolsk. The water quality in different parts of the river according to the contamination index corresponded to the 4-7 grade from "polluted" to "extremely dirty".

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