Transboundary aspects of river water pollution and water quality estimation of the Middle Ob river

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Abstract. The Middle Ob is the part of the Ob river reach running through the central part of Western Siberia within Khanty-Mansi Autonomous Okrug, and brings its waters through the territory of Yamalo-Nenets Autonomous Okrug to the Gulf of Ob of the Arctic Ocean. The data on hydrochemical characteristics of the Middle Ob river and its anabranches during 2003-2008 and 2014-2018 in aspects of transboundary transfer is presented in the article. Composition of salt, organic compounds, heavy metals, petroleum hydrocarbons, biogenic ions in water and bottom sediments are described. The influence of oilfields and urban territories in water catchment area of the Middle Priobie is revealed. The main pollutants of the Middle Ob river are phenols, hydrocarbons, iron, manganese, chrome, copper, phosphate-ions from technogenic and natural originating. We investigated that the level of the Middle Ob river water pollution was increased from 2003-2008 till 2014-2018.

1. Introduction
The Middle Ob is the part of the Ob river reach running through the central part of Western Siberia. In this article we describe the Middle Ob river within Khanty-Mansi Autonomous Okrug. It has a lot of anabranches and inflowing streams draining boggy parts of water catchment area, such rivers as Lyamin, Pim, Tromjegan, Agan are situated on right bank, Bolshoy Yugan, Yuganskaya Ob on left bank.

Density of industrial objects is very high in the water catchment area. This region is the part of the West Siberian oil basin. There are large territories of oilfields and extended oil and gas pipelines, and manufactural infrastructure of biggest in Russia oil producers, such as «Surgutneftegaz», «Rosneft», «LUKoil», «Yuganskneftegaz», «Salym Petroleum Development N.V.» etc. Furthermore, there are more than ten urban settlements in the Middle Priobie basin, the biggest are Surgut, Nizhnevartovsk, Kogalym, Nefteyugansk. Therefore, the anthropogenic loading on the Middle Ob water catchment area is very intensive. It has considerably increased from the middle of the 20th century.

The Middle Ob river brings its waters through the territory of Yamalo-Nenets Autonomous Okrug to the Gulf of Ob of the Kara Sea. So that, we consider the Middle Ob river pollution to have transboundary aspects for Arctic water bodies.

Being the most economically developed region in Russia, the Middle Priobie basin is in a focus of attention of researchers from various scientific fields. Famous scientists from Tomsk, Yekaterinburg, Tyumen, Surgut, Moscow, Sant-Peterburg were studied various aspects of ecological conditions of the
Middle Ob area [1-10]. Our investigation was created from 2003 until the present, and we give an idea of water quality change in dynamics and we consider spatial aspects.

2. Study sites and methods
The objects of our research were the Middle Ob river and its anabranches within Khanty-Mansi Autonomous Okrug. The schematic map of the region of investigation is presented in the figure 1. Samples of water and bottom sediments were collected in 21 control points during 2003-2008 and 26 control points during 2014-2018 on the site of the Middle Ob more than 180 km long during various hydrological seasons.

![Figure 1. The schematic map of the region of investigation (the Middle Ob river with anabranches, 186 km)](image)

The samples of water and bottom sediments were collected according to federal standards adopted in Russia. The samples were analyzed by standard methods of water chemistry, such as titrimetric analyses for chloride-ions and biochemical oxygen demand (BOD), potentiometry for pH, spectrophotometry for biogenic ions and anionic surfactants, fluorimetric method for phenols and oil hydrocarbons, atomic-and-adsorptive spectroscopy for metals. We used water extract of bottom sediments to analyze salts composition, and we investigated total forms of heavy metals. Then we processed the obtained data by methods of mathematical statistics.

3. Results and discussion
Obtained data on chemical composition of water samples collected from the Middle Ob river and its anabranches during 2003-2008 and 2014-2018 is presented in the table 1.

- **pH.** The average pH values are typical for water of the Middle Ob and it is coordinated with results of other researchers [4-8]. However, we obtained several extreme values, which are out of the range of standard values. Subacidic and acidic pH values are usually forms in the inflows of Ob proceeding on boggy sites of the water catchment area. Transition of pH to alkaline values in three samples of water collected during winter is noted. Such pH values indicate anthropogenic loading on the river.

- **BOD.** BOD is an indicator of easily oxidized organic substances content in water. It usually has natural origin. We obtained the values of BOD exceeding standards in 6 samples of water collected during 2003-2008 and in 21 samples collected during 2014-2018. Perhaps it is caused by influence of the urban territories where dumping of municipal sewage is carried out. In general, the level of organic matter contamination was increased till 2003-2008 to 2014-2018.

- **Composition of salts.** The obtained concentrations of chloride ions in the Middle Ob river are below MPC during the research. However, as it mentioned by various researchers, typically concentrations of chlorides in undisturbed rivers in the Middle Priobie usually not more than 20 mg/dm³ [4-8]. So that, in 8 samples of water collected during 2003-2008 and in 3 samples collected during 2014-2018 we obtained the chloride concentrations exceeding background concentration in two and more times. The saline pollution of the Ob river is caused by salty bottom waters from oilfields,
which get on the water catchment area as a result of accidents on pipelines. Concentrations of sulfate ions was low during the entire period of research and didn't exceed MPC.

| Parameter               | Concentration of parameter in water samples collected from the Middle Ob river and anabranches |
|-------------------------|-------------------------------------------------------------------------------------------------|
|                         | 2003-2008 (71 samples)  | 2014-2018 (101 samples) |
| pH                      | Cmin | Cmax | Caverage | Cmin | Cmax | Caverage |
| BOD, mg/dm³             | 3.00 | 0.26 | 6.76      | 2.47 | 0.10 | 122.7     |
| Cl⁻, mg/dm³             | 300.0| <10  | 122.7     | <10  | 56.01| 16.33     |
| SO₄²⁻, mg/dm³           | 100.0| <10  | 18.23     | <10  | 18.23| 12.03     |
| NH₄⁺, mg/dm³            | 0.50 | 0.16 | 3.26      | 1.35 | 0.10 | 0.76      |
| NO₂⁻, mg/dm³            | 0.02 | <0.02| 0.11      | <0.04| 0.12 | 45.81     |
| NO₃⁻, mg/dm³            | 40.00| <0.34| 7.37      | 1.04 | 0.12 | 19.12     |
| PO₄³⁻, mg/dm³           | 0.20 | <0.05| 1.78      | 0.47 | 0.17 | 0.35      |
| Dissolved oxygen, % sat. |      |      | 11.4      | 40.4 | 45.0 | 86.3      |
| Oil hydrocarbons, mg/dm³| 0.50 | 0.01 | 0.149     | 0.048| 0.01 | 0.842     |
| Phenols, mg/dm³         | 0.0010|<0.0005|0.0817|0.00068|<0.0005|0.0270|
| Anionic surfactants, mg/dm³| 0.100|<0.025|0.130|0.053|<0.025|<0.025|
| Fe, mg/dm³              | 0.10 | 0.18 | 6.93      | 2.80 | 1.04 | 4.12      |
| Mn, mg/dm³              | 0.0100|0.0407|0.2308|0.0864|0.086|0.220      |
| Zn, mg/dm³              | 0.0100|0.0224|0.0659|0.0446|<0.005|0.0100|
| Cr, mg/dm³              | 0.0200|0.0005|0.003 | 0.0014|0.0210|0.0490|
| Cu, mg/dm³              | 0.0010|0.0032|0.0086|0.0005|0.0011|0.0049|
| Ni, mg/dm³              | 0.0100|0.0018|0.0033|0.0024|0.0044|0.0097|
| Hg, mg/dm³              | 0.0001|      |<0.0001|<0.0001|<0.0001|<0.0001|
| Pb, mg/dm³              | 0.0060|0.0004|0.0012|0.0007|      |          |

Table 1. Chemical composition of water samples collected from the Middle Ob river

MPC* in rivers for fishery in Russia

| Parameter | Concentration of parameter in water samples collected from the Middle Ob river and anabranches |
|-----------|-------------------------------------------------------------------------------------------------|
| pH        | 6.5-8.5                                                                                           |
| BOD, mg/dm³ | 3.00                                                                                          |
| Cl⁻, mg/dm³ | 300.0                                                                                          |
| SO₄²⁻, mg/dm³ | 100.0                                                                                          |
| NH₄⁺, mg/dm³ | 0.50                                                                                          |
| NO₂⁻, mg/dm³ | 0.02                                                                                          |
| NO₃⁻, mg/dm³ | 40.00                                                                                          |
| PO₄³⁻, mg/dm³ | 0.20                                                                                          |
| Dissolved oxygen, % sat. | 11.4                                                                                          |
| Oil hydrocarbons, mg/dm³ | 0.50                                                                                          |
| Phenols, mg/dm³ | 0.0010                                                                                        |
| Anionic surfactants, mg/dm³ | 0.100                                                                                          |
| Fe, mg/dm³ | 0.10                                                                                          |
| Mn, mg/dm³ | 0.0100                                                                                         |
| Zn, mg/dm³ | 0.0100                                                                                         |
| Cr, mg/dm³ | 0.0200                                                                                         |
| Cu, mg/dm³ | 0.0010                                                                                         |
| Ni, mg/dm³ | 0.0100                                                                                         |
| Hg, mg/dm³ | 0.0001                                                                                         |
| Pb, mg/dm³ | 0.0060                                                                                         |

a Maximum permissible concentration, standards of chemicals contents in waterbodies existing in Russian Federation.
b The empty cell means that data are absent.
c Values which exceed MPC are emphasized.

Biogenic ions are originated in rivers by microbial community because of organic matter transformation. It also comes to water bodies with sewage. One more source of biogenic ions in the Middle Priobie is oil and gas industry. Phosphate ions are one of the component of drill fluids. Obtained data on the biogenic ions concentrations demonstrates that the level of water pollution was higher during 2003-2008. The concentrations of ammonium ions and nitrite ions exceeded MPC to 6 times, the concentrations of phosphates – to 9 times. However, high concentrations of ammonium and nitrite ions in the Middle Ob may be caused by the oxygen deficiency, which was mentioned during our research in 100% of samples. More than 80% of samples of water has the dissolved oxygen concentrations low than 50% saturation. In general, the situation of deficiency of oxygen typically for rivers in taiga landscapes, with the maximum manifestation in the period of a winter, is revealed.
The main industrial pollutants of rivers in the Middle Priobie are oil hydrocarbons, phenols and anionic surfactants. Their significant sources are oilfields and pipelines both as a result of normal operation and especially of accidents [6, 8]. The obtained data on concentration of oil hydrocarbons shows the high level of local oil pollution. We revealed 7 samples of water collected in 2003-2008 exceeded MPC of oil hydrocarbons up to 3 times, and 9 tests in 2014-2018 exceeded MPC up to 16 times. Such concentrations of hydrocarbons in rivers in the Middle Priobie are anomalous, as it revealed by D Moskovchenko [6]. According to the obtained data, the intensity of oil pollution of the Middle Ob river was increased from 2003-2008 till 2014-2018.

The concentration of phenols during 2003-2008 in 4 samples of water reached to 4 values of MPC. As soon as during 2014-2018 we revealed high level of phenol pollution in 31 samples of water where the concentration of phenols exceeded MPC up to 27 times. Phenol compounds may be caused by natural reasons too, such as to the rivers of products of decomposition of leaf litter, wood and needles from water catchment area. However, sharp increase of intensity of phenolic pollution of the Middle Ob till 2003-2008 to 2014-2018 allows to assume its anthropogenic origin. The most intensive phenolic pollution is noted on the site of Ob higher up Surgut in the neighborhood of Langepas.

The concentrations of anionic surfactants were low and stable during the research. It was revealed only 2 samples of water collected during 2003-2008 where the concentrations of pollutant slightly exceeded MPC. During 2014-2018 concentrations of anionic surfactants in water samples were below the detection limit of method.

The concentration of metals in samples of water in 2003-2008 are decreasing in a range: Fe < Mn < Zn < Cu < Ni < Cr < Pb, and in 2014-2018: Fe < Mn < Cr < Zn < Ni < Cu < Hg. Such character of distribution of metals is coordinated with the range of metals in Earth crust [11]. So that, we explain high concentrations of metals in water samples mainly by natural reasons. In condition of acidic pH in taiga landscapes polyvalent cations of metals become soluble and are drained away from soils into water bodies. We obtained extremely high concentrations of ferrum and manganese exceeded MPC in 100% of samples of water. Some increase of concentration of zinc and copper in samples of water collected in 2003-2008 can be caused by the anthropogenic reasons. Concentrations of lead in samples of water were low and stable. Concentrations of mercury in samples of water were below the detection limit of method.

During 2014-2018 we also collected samples of bottom sediments, the obtained data on its chemical composition is presented in the table 2.

| Parameter                        | Concentration of parameter in bottom sediments collected from the Middle Ob river and anabanches during 2014-2018 (40 samples) | C_{min} | C_{max} | C_{average} |
|----------------------------------|--------------------------------------------------------------------------------------------------|--------|--------|-------------|
| pH                               |                                                                                                  | 5.19   | 6.31   | 5.94        |
| Cl\(^-\), mg/kg                  |                                                                                                  | 30.3   | 58.82  | 50.57       |
| SO_4^{2-}, mg/kg                 |                                                                                                  | <120.0 | <120.0 | <120.0      |
| Organic matter, mg/kg            |                                                                                                  | <10000 | <10000 | <10000      |
| Oil hydrocarbons, mg/kg          |                                                                                                  | 54.10  | 81.23  | 68.75       |
| Fe, mg/kg                        |                                                                                                  | 1238   | 2308   | 1484        |
| Mn, mg/kg                        |                                                                                                  | 76.3   | 171.5  | 127.7       |
| Zn, mg/kg                        |                                                                                                  | 3.26   | 6.38   | 4.95        |
| Cr, mg/kg                        |                                                                                                  | 1.9    | 2.8    | 2.4         |
| Cu, mg/kg                        |                                                                                                  | <1.5   | <1.5   | <1.5        |
| Ni, mg/kg                        |                                                                                                  | 2.9    | 6.8    | 5.21        |
| Hg, mg/kg                        |                                                                                                  | 1.1    | 14.4   | 8.07        |
| Pb, mg/kg                        |                                                                                                  | 7.04   | 8.94   | 7.97        |
The chemical composition of bottom sediments is typical for the Middle Ob. These are the alluvial deposits, with the low content of salts and organic substance, and acid рН values. Concentration of hydrocarbons exceeded the Maximum Permissible Level (MPL) of content of oil and oil products in bottom sediments of surface water objects in the territory of Khanty-Mansi Autonomous Okrug (20 mg/kg) in 2.7-4.0 times. It confirms an accumulative role of bottom sediments and accumulation in them of technogenic pollutants.

The concentrations of metals in samples of bottom sediments are decreasing in a range: Fe < Mn < Hg < Pb < Ni < Zn < Cr < Cu. The order of distribution of metals in this range does not coordinate with that range neither for water samples nor for Earth crust. Except for iron and manganese, which also take the first positions in the range both for water and for Earth crust. However, concentrations of metals in the bottom sediments are much lower in comparison with the content in Earth crust. Location of mercury, lead and nickel among metals allow to assume their technogenic origin.

4. Conclusion
The main pollutants of the Middle Ob river are phenols, hydrocarbons, iron, manganese, cooper, phosphate-ions from technogenic and natural originating. Several indicators of technogenic loading on the Middle Ob river were revealed during our research. Such as transition of рН to alkaline values, high concentrations of phosphate-ions and phenols in water samples, anomalous high concentrations of oil hydrocarbons in water and bottom sediments, location of mercury, lead and nickel in the range of metals in the bottom sediments. We also identified the accumulative role of bottom sediments and accumulation in them of technogenic pollutants.

It can be mentioned that during 2003-2008 we evaluated the higher level of river water pollution by the biogenic ions, and the level of organic matter contamination was increased till 2003-2008 to 2014-2018, including oil hydrocarbons and phenols. However, it is local pollution, the most intensive polluted sites of the Middle Ob are noted higher up Surgut in the neighborhood of Langepas.

The Middle Priobie is an outpost of the Arctic. The Arctic water ecosystems are very vulnerable to pollution because of low ability to self-cleaning. To ensure environmental safety of the Arctic water areas it is necessary to conduct continuous environmental monitoring of the Middle Ob river and its anabranches and inflowing streams.

References
[1] Kukurichkin G and Babyuk S 2014 23rd Int. Workshop of the Europ. Vegetation Survey (Ljubljana: ZRC Publishing House) p 133
[2] Sofronova E, Afonina O, Andreeva E, Beldiman L, Bezgodov A, Borovichev E, Boiuchuk M, Chepinoga V, Chernjadieva I, Doroshina G et al 2016 Arctoa 25 vol 1 pp 183-228
[3] Shornikova E 2008 Contemp. Probl. of Ecology 1 vol 3 pp 328-34
[4] Shornikova E 2007 Biolog. Res. and Environ. Management 10 ed G Kukurichkin (Surgut: Defis) pp 253-56
[5] Moiseenko T 2018 Environ. Res. Lett. 13 105007
[6] Moskovchenko D, Babushkin A 2014 Ecology and Industry of Russia 4 pp 34-38
[7] Moskovchenko D, Babushkin A and Ubaidulaev A 2017 Water res. 44 vol 1 pp 91-102
[8] Babushkin A, Moskovchenko D and Pikunov S 2007 Hydrochemical Monitoring of the Surface Waters in Khanty-Mansi Autonomous Okrug – Ugra ed V Tsibulsky (Novosibirsk: Nauka)
[9] Soromotin A 2011 Contemp. Probl. of Ecol. 4 vol 6 pp 600-607
[10] Mikhailova L, Uvarova V and Barkhovich O 1988 Water res. 3 pp 25-35
[11] Vinogradov A. 1962 Geochemistry 7 pp 555-571