Analysis of Spatial Variability of Water Chemistry Indicators of the Rivers within Oilfields of Khanty-Mansi Autonomous Okrug – Ugra

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Abstract. An increase of technogenic load on the catchment area with a decrease of the volume of water protection measures leads to spread of surface water pollution. The paper considers the chemical composition of surface waters in Khanty-Mansi autonomous okrug – Ugra. The technique for analyzing the chemical composition of surface waters based on the combined application of the method of cluster analysis is presented. In this work, the concentration of metal ions in the rivers under study was determined. It was found that concentrations of iron and zinc ions exceeded the maximum permitted concentrations for fishery rivers (MPC) in 100% of samples, as for copper concentration an excess of MPC was noted in some cases. The spatial dynamics of the distribution of chlorides and oil hydrocarbons in surface waters is considered. According to the monitoring data, the analyzed surface water samples had very low concentrations of chlorides and oil hydrocarbons.

1. Introduction
The chemical composition of surface waters is the result of complex multi-stage processes occurring both in the catchment area and in the water body itself. The main natural sources of entry of chemical substances into the aquatic environment are rock weathering in the catchment, release from bottom sediments, fallout from the atmosphere, mineralization of organic matter in the catchment and in the water body itself.

Khanty-Mansi Autonomous Okrug – Ugra is one of the most dynamically developing regions of Russia with a huge and diverse natural resource potential. The ecological situation in the region is formed under the influence of the national economy on the environment, predominantly of the oil and gas production complex as the basis of the economy of Ugra. In addition, severe industrial factors of landscape’s transformation in the region are expanding of pipeline infrastructure for crude oil and natural gas transportation, operating of large power plants, constructing of long-distance transmission circuit, timber harvesting etc.

Due to flows of natural and anthropogenic substances pass through hydrographic network, it is considered to be the main part of landscape-geochemical studies. The dynamics of chemical composition of surface waters is significant indicator of regional environmental state. Therefore,
hydrochemical researches constitute the most important section of the territorial system of environmental monitoring of Ugra. Last decades a number of researches concerned to surface water quality were carried out in Khanty-Mansi Autonomous Okrug – Ugra [1-7]. Our study deals mostly with minor rivers within oilfields. The main purpose of this research was to categorize rivers according to chemical composition by the technique of cluster analysis.

2. Study sites and methods
The objects of research were surface water of rivers located within oilfields in Khanty-Mansiysk Autonomous Okrug (Table 1).

| Site number | Site location | Administrative area | River          |
|-------------|---------------|---------------------|----------------|
| P1          | 61°40'31"N 72°48'45"E | Surgut             | Vynga          |
| P2          | 61°26'17"N 72°42'02"E | Minchimkina        |                |
| P3          | 61°37'49"N 72°51'50"E | Minchimkina`s right bank inflow |                |
| P4          | 61°25'01"N 72°45'19"E | Bystryi Kul`egan    |                |
| P5          | 61°19'35"N 72°27'19"E | Kavyk              |                |
| P6          | 61°58'03"N 72°36'19"E | Tap`yaun           |                |
| P7          | 61°55'42"N 72°46'32"E | Yak`yavin          |                |
| P8          | 61°26'24"N 72°15'22"E | Komar`ya           |                |
| P9          | 61°28'50"N 72°10'28"E | Virsiyavin         |                |
| P10         | 61°28'37"N 72°07'59"E | Pim                |                |
| P11         | 61°04'46"N 67°19'34"E | Oktyabrsky         | Ob             |
| P12         | 62°10'45"N 67°10'31"E | Bolshaya Leushinskaya |                |
| P13         | 62°05'57"N 67°30'08"E | Malay Leushinskaya |                |
| P14         | 62°04'00"N 67°30'35"E | Bolshaya Karymkarskaya |                |
| P15         | 62°22'24"N 67°02'28"E | Malay Karymkarskaya |                |
| P16         | 62°19'40"N 67°11'44"E | Kurnisoim          |                |
| P17         | 62°24'51"N 67°13'27"E | Bolshoy Okhtach    |                |
| P18         | 62°06'10"N 67°23'37"E | Khompa             |                |
| P19         | 62°05'57"N 67°30'08"E | Mal`yi Atlym       |                |
| P20         | 62°20'03"N 67°12'07"E | Ovyn`egan          |                |

Water sampling and conservation were carried out according to federal standards adopted in Russia. Samples of water were collected during navigation season of 2018-2019. The data on the concentration of metal ions (Fe, Mg, Cu, Pb, Ni, Hg, Cr, Zn), chloride ions and oil hydrocarbons was used to distinguish spatial differences in chemical composition of river water by the technique of cluster analysis [8]. The samples were analyzed by standard methods of water chemistry, such as titrimetric analyses for chloride ions, fluorimetric method for oil hydrocarbons, atomic-and-adsorptive spectroscopy for metals.

3. Results and discussion
Heavy metals are particularly harmful to aquatic ecosystems and hydrobions. They belong to the conservative pollutants that do not decompose in natural waters, but only change the form of their existence, remain in water bodies for a long time even after the source of pollution is removed.

According to obtained data, consistently high concentrations of iron and zinc exceeding the MPC for fishery rivers were revealed in minor and medium rivers both of Surgut and Oktyabrsky area. It is associated with the regional features, as the formation of the chemical composition of surface waters occurs in the conditions of high degree of swamping of West Siberian plain. Swamp waters are
characterized by a large amount of organic matter, high acidity and oxidizability. Therefore, the influence of swamps largely determines the regional features of the river waters of the Khanty-Mansi autonomous okrug.

The normalized data of average values of concentrations of heavy metals received during 2018-2019 were processed using method of cluster analysis (fig.1). In the resulting groups by clusters for metals in studied rivers, two cascade systems can be distinguished, differing in the concentration of hydrochemical indicators and the degree of environmental load:

1) rivers of Surgut area (P1-P6, P8-P10);
2) rivers of Oktyabrsky area (P7, P11-P20).

![Figure 1. The result of the cluster analysis of the concentrations of metals, grouped by sampling sites.](image)

The first cascade system includes all the studied rivers of Surgut area with the highest concentration of metals. On the one hand, high concentrations of metals in water samples could be caused 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 [1]. On the other hand, anthropogenic activity leads to an increase in the level of metals in natural waters due to landscape transformation during construction and development of oilfields.

The second group with a satisfactory environmental conditions consists from the rivers of Oktyabrsky area, and also the Yak’yavin river of Surgut area. Relatively low concentration of metals in Oktyabrsky area statistically proves the predominance of nature sources in formation of metal compounds in the surface waters. Thus, Surgutskoe Polesie is characterized by an unprecedented degree of swampliness, which is much more than in Oktyabrsky area.

The concentrations of oil hydrocarbons and chloride ions in surface waters have particular relevance for estimation of the ecological conditions in the region, since characterize industrial flows of pollutants in the areas of oilfields. Obtained data demonstrates sustainable environmental conditions within oilfields as the concentration of industrial pollutants in studied rivers does not exceed natural background concentration of chloride ions and oil hydrocarbons in undisturbed rivers. The concentrations of these indicators are decreasing annually, in our research they are below the MPC for oil hydrocarbons (from 0.03 to 0.046 mg/dm³), and for chloride ions they are hundredths of the MPC for fishery rivers.
Figure 2. The results of cluster analysis of the concentrations of chloride-ions and oil hydrocarbons grouped by sampling sites.

According to Fig. 2, two clusters can be distinguished, combining rivers with the maximum and minimum values of chloride ions:

1) P2, P4, P6 – the concentrations of chloride ions are 16–20.6 mg/dm³;
2) P3, P5, P7, P10, P12–20 – the concentration of chloride ions does not exceed 10 mg/dm³.

4. Conclusion
The studied rivers were characterized with high concentrations of metals. The value of iron exceeded MCP for fishery rivers in 100% of samples. High concentrations of cooper were revealed sporadically in several samples. On the results of cluster analysis, the rivers were categorized into two groups according to the content of metals. The first group consisted from the rivers within oilfields of Surgut area with high value of metals. The second group included mostly the rivers of Oktyabrsky area with less concentrations of metals. It statistically proves that the main reasons of highly metalized waters are natural processes occurring in swamped catchment area which transform metal compounds into soluble forms and allow them to drain into water bodies.

The concentrations of industrial pollutants from oil producing processes were comparable to natural background concentrations in undisturbed rivers of Khanty-Mansi autonomous okrug. All the samples had low concentrations of oil hydrocarbons and chloride ions, not exceeding MPC for fishery rivers. Investigated rivers were also divided into two clusters according to chloride ion concentrations.

As rivers are illustrative indicator of the ecological state of the catchment area, we consider the environmental conditions on the oilfields of Khanty-Mansi autonomous okrug – Ugra to be sustainable.

5. References
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