Application of the comprehensive analysis of pollution of the Kacha river by oil products in the information and analytical system

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Abstract. This article examines the analysis of the concentration of oil products depending on the anthropogenic impact on water quality in the Kacha River. As part of the work, the regularities of the dynamics of changes in the concentration of oil products in the Kacha River in the period from January 2014 to December 2020 were investigated, methods for determining oil products in water were considered, and one of them was selected for analyzing the pollution of the Kacha River. An analysis was also carried out between the concentrations of oil products and other pollutants controlled at this facility. A method of cleaning from petroleum products has been selected. The experimental research technique is described, the results are presented in the form of tables and diagrams. A prototype of an information and analytical system for analyzing the concentration of oil products in water basins has been designed.

1. Introduction

The quality of drinking water is the main environmental problem of mankind, which directly affects the health of the population and the ecological purity of consumed products.

Most of the water is concentrated in the seas and oceans of our planet. Fresh water accounts for only about 2%. Recently, there has been an acute shortage of fresh water. Already, about a third of the Earth lacks clean fresh water. The increased water shortage is also associated with the pollution of water bodies with industrial and domestic wastewater.

Anthropogenic impacts on the hydrosphere include two aspects: water pollution and depletion of surface and groundwater. The pollution of water bodies is understood as a decrease in their biospheric functions and ecological significance as a result of the intake of harmful substances into them. More than 400 water pollutants have been identified. There are many indicators that pollute surface waters. These can be various metals, radioactive substances, pesticides, organic substances [1].

The deterioration of the environmental situation in the country and the Krasnoyarsk territory in particular has led to the need for state monitoring in areas with increased anthropogenic impact, including in the form of laboratory and analytical work with water sampling, while providing information support and interaction with all participants in monitoring water objects in the region.

In the Krasnoyarsk territory, a set of all necessary measures is being implemented to improve the quality of the environment and reduce the negative impact of the industrial centers of the region. In particular, the territory of the region continues to implement the concept of the regional environmental policy until 2030, control is carried out under the program "Reducing the negative impact on the
environment by enterprises of the Krasnoyarsk territory for 2014-2020, as well as the procedure for the operation of enterprises during unfavorable weather conditions in Krasnoyarsk [2].

To automate and reduce the time spent on data collection and analysis, it is necessary to develop a system that will allow accumulating, systematizing and visualizing information on the concentration of oil products.

To implement a set of measures to improve the quality of the environment on the territory of the Krasnoyarsk territory, observations are carried out over the pollution of surface waters of the land according to hydrological and hydrochemical indicators.

Regular monitoring of water pollution in the river Kacha were carried out at two observation points: above the city of Krasnoyarsk and within the city of Krasnoyarsk. The most common pollutants for this object are phenols, oil products, metal compounds: general iron, aluminum, copper, manganese, zinc.

The purpose of this work is to monitor up-to-date information on the content of oil products in the Kacha River using an information-analytical system and proposals for eliminating the consequences of pollution.

2. Methods

Methods for measuring the mass concentration of petroleum products in samples of drinking, natural and treated wastewater by infrared spectrophotometry using concentrators.

Measurement range from 0.02 to 2 mg/dm³.

The interfering influence of other substances present in the water sample is eliminated during the sample preparation process.

The measurement of the mass concentration of petroleum products in samples of drinking, natural and treated wastewater is carried out by the infrared spectrophotometric method [3,4,5].

The method for measuring the mass concentration of oil products is based on the dependence of the intensity of absorption of bonds in the infrared region of the spectrum (2930 ± 70) cm⁻¹ on the mass concentration of oil products in the solution.

The reagents used must be "chemically pure". It is allowed to use reagents of "analytical grade" grade. The list of reagents and solutions used with a description of their brand, preparation, use, conditions and shelf life corresponds to the methodology.

The used laboratory measuring glass complies with the requirements of the method.

2.1. Preparing a chromatographic column

A layer (~ 0.5 cm) of glass wool is placed in the bottom of the washed and dried column. Then 3 grams of alumina are poured into the chromatographic column, and the glass wool layer is again placed. Pass through the column 10 cm³ of carbon tetrachloride. The first portion of the carbon tetrachloride eluate (~ 3 cm³) passed through the column is discarded. The next portion of the eluate is collected in a clean beaker. The measuring cuvette is preliminarily rinsed with a small amount of eluate, then it is filled and the mass concentration of oil products in the eluate is measured.

If the measured value of the mass concentration of oil products in the eluate on the device does not exceed 0.6 mg/dm³, then the chromatographic column is suitable for operation. If the specified value is exceeded, the chromatographic column is washed again with a new portion of carbon tetrachloride and the measurement is repeated.

2.2. Extraction

A sample of the analyzed water is completely transferred into a separating funnel of appropriate capacity and sulfuric acid is added until pH ~ 2.

If the water sample has been previously preserved, no sulfuric acid is added.

Then 40 grams of sodium chloride was added per 1 dm³ of water sample. The container containing the sample is thoroughly rinsed with 5 cm³ of carbon tetrachloride and poured into a separatory funnel. Add another 5 cm³ of carbon tetrachloride there.
Extraction is performed using a laboratory extractor for at least 5 minutes at a stirrer rotation speed of ~ 2500 rpm./min. When carrying out extraction, it is necessary to ensure that the extractant is evenly distributed over the entire volume of the water sample, then the water sample is defended for (10 - 15) minutes to separate the aqueous and organic phases.

After phase separation, the lower layer (extract) is poured into a conical flask with a ground stopper and processed or left for storage. The shelf life of extracts should not exceed 10 months. After separating the extract, the volume of the analyzed water sample is measured with a graduated cylinder. When carrying out extraction using a laboratory extractor, they are guided by a passport. In the absence of a laboratory extractor, it is allowed to carry out extraction in a separating funnel by shaking the water sample for 10 minutes.

2.3. Extract processing
The extract is dried with sodium sulfate for 10 minutes, adding it to the glass in small portions, stirring the contents with a glass stick. After completion of the drying process, the extract is poured into a measuring cylinder with a capacity of (10 - 25) cm$^3$. 3 cm$^3$ of carbon tetrachloride is poured into the prepared chromatographic column for wetting. As soon as the tetrachloride is absorbed into the alumina, the extract is passed through a chromatographic column. Care must be taken to ensure that the liquid level does not fall below the upper layer of aluminum oxide. The first 3 cm$^3$ of the eluate is discarded, the rest of the eluate is collected in a flask with a ground stopper.

2.4. Taking measurements
Measurements are carried out in accordance with the concentrometer operating manual. The measuring cuvette is preliminarily rinsed with a small amount of eluate, and then the cuvette is filled with it. Install the cuvette into the device and measure the mass concentration of oil products in the eluate, reading the readings of the device.

If the mass concentration of oil products exceeds the upper limit of the measuring range of the device, then the eluate is diluted with carbon tetrachloride. Then the solution is poured into a cuvette, which is preliminarily rinsed with this solution, installed in the device and measured.

2.5. Determination of oil products in a blank sample
Before analyzing a series of samples, determine the mass concentration of oil products in a blank sample. To do this, take 1 dm$^3$ of distilled water and process it as a sample. Measure the mass concentration of oil products in the eluate.

If the measured value of the mass concentration of oil products in the eluate is negative, then it is necessary to purify carbon tetrachloride. Then repeat the procedure for preparing the solutions and carry out the installation of the initial values.

If the measured value of the mass concentration of oil products in the blank sample exceeds 0.02 mg / dm$^3$, then the determination is repeated and, if necessary, the cause of contamination of the blank sample is identified and eliminated.

Blank analysis is also performed when using a new batch of reagents. The results of the analysis of the blank sample are taken into account when calculating the mass concentration of oil products in the sample [6,7].

2.6. Processing of measurement results
The measurement result is the mass concentration of oil products in the water sample, X, mg / dm$^3$, calculated according to formula 1.

$$X = \frac{X_{izm} V_{ek} K}{V} - X_{HOL}$$

(1)
where $X_{IZM}$ - is the result of measurements of the mass concentration of oil products in the eluate using a concentrometer, mg / dm$^3$;

$V_{EK}$ - volume of carbon tetrachloride used for extraction ($V_{EK}=10$ cm$^3$);

$K$ - dilution factor, i.e. the ratio of the volumes of the volumetric flask and the aliquot of the eluate;

$V$ - sample volume of analyzed water, cm$^3$;

$X_{HOL}$ - the result of measurements of the mass concentration of oil products in the blank sample in terms of the volume of the distilled water sample, mg / dm$^3$.

The measurement result is the mass concentration of oil products in the blank sample, $X_{HOL}$, mg / dm$^3$, calculated by formula 2.

$$X = \frac{X_{IZM} \cdot V_{EK}}{V}$$

(2)

The result of the analysis of the mass concentration of oil products is the result of a single measurement.

3. Results

For the analysis, the database on the concentrations of pollutants of the FGBU "Central Siberian UGMS" and the KGBU "CRMP and OOS" was used in the period from January 2014 to December 2020.

During the study period, the data on the concentration of oil products in water were analyzed. A total of 168 samples were analyzed. Of these, the excess of maximum permissible concentrations was observed in 41 samples. The number of analyzed samples is due to the fact that during the year, every month in the Kacha River, samples were taken at two points.

The background point was taken above the city limits, before the anthropogenic load, above the village of Yemelyanovo. The second point under study was taken within the city of Krasnoyarsk, 4.5 km below the confluence of the Bugach River.

The following is table 1 showing the number of samples analyzed and the number of times the maximum allowable concentration (MPC) was exceeded annually.

Petroleum products are a substance of hazard class 3, MPC = 0.05 mg / m$^3$.

| Year | 2014 | 2015 | 2016 | 2017 | 2018 | 2019 | 2020 |
|------|------|------|------|------|------|------|------|
| Number of samples analyzed | 24 | 24 | 24 | 24 | 24 | 24 | 24 |
| The number of samples exceeding the MPC | 9 | 5 | 5 | 7 | 7 | 4 | 4 |

Taking into account the fact that the values of the concentration of oil products at the background point were always below the detection limit, the existing excesses correspond only to a point within the city limits. According to the data obtained, we see that the number of samples exceeding the MPC for petroleum products has almost halved by 2018. And in 2014, we observe the maximum number of overshoots during the study period.

| Month   | 2014 | 2015 | 2016 | 2017 | 2018 | 2019 | 2020 |
|---------|------|------|------|------|------|------|------|
| January | 0.06 | 0.00 | 0.11 | 0.04 | 0.2  | 0.00 | 0.00 |
| February| 0.08 | 0.00 | 0.10 | 0.00 | 0.06 | 0.05 | 0.00 |
| March   | 0.09 | 0.14 | 0.00 | 0.24 | 0.07 | 0.00 | 0.00 |
From table 2 we see that for the entire considered period in the month of May, there was not a single value that would be below the detection limit. This allows us to assume that all pollutants accumulated during the winter, including oil products, enter the river with melt water.

Based on the data obtained, diagrams were drawn up for clarity of dynamics and further analysis. Next, we will consider the diagrams of changes in the concentration of oil products for each year of the studied period based on the table of the results of the analysis of water samples from the Kacha River within the city, shown in figure 1.

### Table 2: Concentration of Oil Products in Water Samples from the Kacha River

| Month    | April | May  | June | July | August | September | October | November | December |
|----------|-------|------|------|------|--------|-----------|---------|----------|----------|
|          | 0.02  | 0.08 | 0.04 | 0.05 | 0.1    | 0.00      | 0.15    | 0.05     | 0.00     |
|          | 0.08  | 0.05 | 0.06 | 0.07 | 0.07   | 0.04      | 0.06    | 0.05     | 0.06     |
|          | 0.21  | 0.00 | 0.20 | 0.05 | 0.27   | 0.15      | 0.00    | 0.10     | 0.09     |
|          | 0.03  | 0.14 | 0.05 | 0.00 | 0.00   | 0.00      | 0.00    | 0.00     | 0.00     |
|          | 0.07  | 0.05 | 0.00 | 0.12 | 0.05   | 0.00      | 0.00    | 0.07     | 0.00     |
|          | 0.07  | 0.00 | 0.05 | 0.19 | 0.07   | 0.06      | 0.07    | 0.00     | 0.05     |
|          | 0.07  | 0.10 | 0.00 | 0.11 | 0.00   | 0.07      | 0.00    | 0.00     | 0.05     |
|          | 0.12  | 0.00 | 0.00 | 0.06 | 0.00   | 0.00      | 0.05    | 0.00     | 0.00     |
|          | 0.02  | 0.00 | 0.06 | 0.00 | 0.00   | 0.00      | 0.00    | 0.00     | 0.00     |

#### Diagrams

**Year 2014**

**Year 2015**

**Year 2018**

**Year 2019**
Based on the data presented in the diagrams in figure 1, it can be concluded that the concentration of oil products during this period of time is not constant. It is not possible to identify the patterns of changes. Each year, the only constant concentrations are those that exceed the maximum permissible concentrations, which are detected in different periods and do not have regularities.

Based on the above methods for analyzing water for oil content, an interface for future information systems was developed.

The main menu of the page is a map on which objects are located: rivers, reservoirs, lakes, etc. By selecting a marker on the map in the place where the object is located, you can find out information about the concentration of substances contained in the water basin of the object (figure 2). And you can also add new objects by pre-defining a point on the map.

**Figure 1.** Diagrams of changes in the concentration of petroleum products for 2014-2020.

**Figure 2.** The interface of the main page of the information and analytical system.
4. Conclusion
In this work, it was considered how oil and oil products have a detrimental effect on many living organisms, and, consequently, on all links of the biological chain. Most oil products easily penetrate the body even through intact skin, causing metabolic disturbances.

The Kacha River was chosen as the object of this study. The background point was chosen above the village of Yemelyanovo, before anthropogenic impact. The second point under study was taken within the city of Krasnoyarsk, 4.5 km below the confluence of the Bugach River.

The paper investigates the dynamics of changes in the concentration of oil products in the Kacha River in the period from January 2014 to December 2020.

An analysis was carried out between the concentrations of oil products and other pollutants controlled at this facility.

On the basis of the studied methods of water purification, an integrated method of purification from oil products was selected.

In the future, it is planned to scale this approach for monitoring other water bodies of the Krasnoyarsk territory.

A prototype of a future information and analytical system for analyzing the concentration of oil products in a water basin is presented.

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