Assessment of the Bottom Sediments State After Oil Spill

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Abstract. The paper has deal with the monitoring of the lake bottom sediments which were contaminated by oil during emergency spill. The results of geochemical study of chloroform bitumoids extracted from sediment samples showed that the processes of transformation of oil hydrocarbons lasted for 10 years since the oil spill. This is indicated a decrease in the residual oil content and changes in the chemical composition of bitumoids. The hydrocarbons content was decreasing and resinous-asphaltene components was increasing as oxygen-containing groups and bonds in the chemical structure of bitumoids. In the individual composition of hydrocarbons the significant redistribution of saturated hydrocarbons was occurring both within the homologous series and between different homologous series, the CPI coefficient and the biodegradation coefficient Prophy/nC₁₇+nC₁₈ was increasing. By 2017 in absence of new oil spills the chemical composition of bottom sediments had closed to a state inherent in the native organic matter of bottom sediments of coastal lake facies, which characterized by the presence of compounds typical for higher plant lipids (dominance of high molecular weight n-alkanes of composition nC₂₃–nC₃₃ with a significant predominance of odd homologues, a high content of oxygen-containing compounds – solid saturated fatty acids, aliphatic esters and saturated ketones).

1. Introduction
With the rapid growth of the oil and gas industry in the Republic of Sakha (Yakutia) the risk of oil pollution of environmental objects increases. The most of the oil and gas fields of the Eastern Siberia located in the taiga zone far from large rivers and seas because small rivers, lakes, streams and other water bodies can be affected, primarily due to emergency situations. There for bottom sediments contaminated with oil and oil products are the subject of many investigations that are related to the study of the specifics of the hydrocarbon geochemical background and technogenic anomalies [1–4]. In general, research has focused on the recognition of the nature and characteristics of the hydrocarbon distribution in bottom sediments in connection with solving the problems of identifying technogenic pollution and assessing its level as studying the features of transformation of the oil hydrocarbons composition [2–9]. During oil spill its components fall into the water, adsorb on surface of suspended particles and then locate in bottom sediments [1, 2]. The processes of oil hydrocarbon adsorption by bottom sediments lead to a decrease their content in water, but under certain conditions they may be a secondary source of water pollution. Most of the spilled oil concentrates mainly along the banks of water bodies, the rest part evaporates and processes by hydrocarbon-oxidizing bacteria.

The processes of transformation of oil hydrocarbons in bottom sediments occur with oxygen deficiency and therefore proceed extremely slowly. In the climatic conditions of the Yakutia, oil
hydrocarbons are accumulated by bottom sediments and can be a source of pollution of water bodies for a long time.

2. Data and methods
The paper discusses the results of many years researches on the dynamics of changes of chloroform bitumen (CB) content and their fractions in the bottom sediments of Lake Taloe, contaminated during the accidental spill at an oil pipeline in 2006 in the Lensky district of the Republic of Sakha (Yakutia). As a result, the surface waters of the Bezymyanny stream with a total area of 71,650 m², Lake Taloe, which has an area of 100,000 m², were contaminated with oil. The research material was based on surface bottom sediments selected in field studies in 2007, 2012, 2015, 2017 in an area with geographical coordinates 59°33′44.5″ N, 112°07′03.3″E. Samples were taken in the direction of the spread of the oil film from the accident site at the mouth of the stream flowing into Lake Taloe, in the lake and at the area where the stream flows from the lake. These water bodies represent a single landscape-geochemical system. The chemical composition of bottom sediments is largely due to the interaction of melt, flood and rainwater with soils. Thus, oil hydrocarbons fell into bottom sediments not only from the water surface, but also from near contaminated territory.

In the samples there were determined a content of chloroform bitumoid (CB) by extraction method as structural-group composition of CB by IR-Fourier spectrometry. IR spectra were recorded on the Nicolet Protege 460 IR-Fourier spectrometer in the wave number range 500–4000 cm⁻¹ in the cell with KBr windows, the thickness of the absorbing layer was 33x10⁻⁴ m. The spectra were interpreted using the atlases of the IR-spectra and the wave number tables [10, 11]. The relative absorption coefficients of carbonyl groups, ether and hydroxyl compounds, which characterize the degree of oil oxidation, were calculated by IR-spectra of CB. Liquid adsorption chromatography was used for fractional separation soil extracts to hydrocarbon, asphaltene and resinous components [12].

The chromato-mass-spectrometric (GC/MS) studies of saturated hydrocarbon fractions of the oil fractions were performed on the system including the gas chromatograph Agilent 6890 with interface and high-performance mass-selective detector Agilent 5973N. The chromatograph is equipped with a quartz capillary column 25 m long, 0.25 mm diameter, impregnated phase HP-5MS. Carrier gas – helium, flow rate 1 ml/min. evaporator Temperature 320 °C; programming temperature rise – from 100 to 300 °C at a speed of 4 °C min⁻¹ followed by isotherm for 30 min. Ionizing voltage source 70 eV, source temperature 220 °C. The mass chromatograms of hydrocarbons (oil fractions) were obtained from total ion current (TIC) and characteristic fragment ions. Identification of individual hydrocarbons was carried out by computer search in the library of the National Institute of Standards NIST-05 according to literature data and reconstruction of structures by the nature of ion fragmentation in electronic impact [13, 14].

Frequency of measurements was triple. Data in the form of arithmetic averages of values are given on drawings and in tables. The received results in comparison with control are statistically reliable.

3. Results and discussion
Since there are no standard values scale for detection of oil contamination level in bottom sediments, in this work we determined a level of contamination of bottom sediments by the content of CB, as well as for soils samples, according to the classification [1]. A year after the accident the average CB content was 107247 mg kg⁻¹ and corresponded to a very high level of pollution (table 1).

It should be noted that the yield of CB increased in the direction of movement of the oil film, the maximum content of CB was recorded in sediments of the stream flowed out of the lake (figure 1c). This may be due to the installation of booms in this place during the oil spill response works, which caused oil accumulation, an increase in oil film thickness and pollution area. The same trend was observed in subsequent 2012 and 2015. At this sampling point, over 10 years of observation, the yield of CB decreased by 79 times. In sediments taken at the mouth of the stream flowed into the lake, the yield of CB was lower than at other sampling points for the entire time of observation (figure 1a). In
sediments of the lake, the yield of CB decreased by 17 times (figure 1b). In general, the average yield of CB over the years of observations decreased to 2705 mg kg\(^{-1}\) (table 1).

| Parameters                              | Sampling year |
|-----------------------------------------|---------------|
|                                         | 2007   | 2012    | 2015    | 2017    |
| Average yield of CB, mg kg\(^{-1}\)     | 107247 | 3168    | 4336    | 2705    |
| Hydrocarbons, %                         | 58.33  | 45.88   | 20.61   | 11.89   |
| Benzene resins, %                       | 12.33  | 15.02   | 6.82    | 6.53    |
| Alcohol benzene resins, %               | 19.15  | 29.59   | 37.36   | 51.30   |
| Asphaltenes, %                          | 15.42  | 9.51    | 34.97   | 30.28   |
| \(\Sigma b.b.t.-nC_{20}/\Sigma nC_{21}-e.b.t\)^a | 1.45   | 0.07    | 0.06    | 0.06    |
| CPI\(^b\)                               | 1.08   | 6.39    | 8.04    | 8.18    |
| Pr/Ph\(^c\)                             | 0.71   | 0.83    | 0.90    | 1.28    |
| Pr+Ph/nC\(_{17}+nC_{18}\)^d            | 1.46   | 3.54    | 3.66    | 1.47    |

\(^a\) b.b.t. temperature of beginning boiling; e.b.t. temperature of end boiling

\(^b\) The ratio of n-alkanes with an odd number of carbons to n-alkanes with an even number

\(^c\) The ratio of pristine over phytane

\(^d\) Sum of pristane and phytane over the sum of n-heptadecane and n-octadecane

According to IR-Fourier spectroscopy, the structural-group composition of CB samples during the considered observation period changed in the direction of an increase in oxygen-containing groups and bonds, as indicated by an increase in the relative absorption coefficients of carbonyl (K\(_{1700}\), K\(_{1740}\)), ether (K\(_{1170}\)) and hydroxyl (K\(_{3300}\)) groups in the spectra of CB samples (figure 2). The coefficients were calculated as the ratio of the optical absorption densities of oxygen-containing groups to methyl and methylene groups (absorption band at 1460 cm\(^{-1}\)). The appearance of the absorption band of carbonyl groups in the region of 1740 cm\(^{-1}\) and hydroxyl groups in the region of 3300 cm\(^{-1}\) was observed only 10 years after the spill (figure 2, figure 3). This may be caused by the processes of biochemical oxidation of petroleum hydrocarbons on the one hand, and on the other - the appearance of an absorption band of 1740 cm\(^{-1}\) may be due to the presence of a significant amount of solid saturated acids inherent bottom sediments of unpolluted water bodies due to the impact of organic matter of higher ground plants.
Figure 2. Change in the relative absorption coefficients of oxygen-containing groups in the IR spectra of CB.

Figure 3. IR-spectra of CB of bottom sediments sampling in: 2007 (a), 2012 (b), 2015 (c), 2017 (d).
During the whole monitoring the group composition of CB bottom sediment samples showed changes towards a decrease in hydrocarbon and an increase in asphalt-resinous components, and in the composition of the latter, the amount of alcohol-benzene resins and asphaltenes (table 1). As can see from the above data, during the transformation of oil in the water reservoir, high molecular weight components accumulated, settled to the bottom and then they were sorbed by sediments [2]. According to the researchers [15], the features of the accumulation of resinous-asphaltic components are closely related to the composition of the sediments and the depth of sampling (the redox environment of the burial). According to the research results, the average content of alcohol-benzene resins and asphaltenes increases during the biodegradation of oil pollution in bottom sediments and the residual accumulation of high molecular weight components (table 1).

To study the processes transformation of oil contamination of bottom sediments, we used the data on chromatography-mass spectrometry of the composition of saturated hydrocarbons CB. It is known that during the transformation of oil hydrocarbons, alkanes are the first to be utilized [16]. Our results showed that the dynamics of changes in the individual composition of saturated hydrocarbons in bottom sediments expressed in a decrease in the content of relatively low molecular weight n-alkanes, an increase in the ratio of n-alkanes with odd number of carbon atoms in the molecule to even number of n-alkanes (CPI) (table 1).

The presence of oil hydrocarbons in sediments was indicated by the ratio of pristan to phytane (Pr / Ph), which until 2015 was less than unity. The ratio of sum Pr and Ph to the sum of eluting n-alkanes (Pr+Ph/nC_{17}+nC_{18}) also indicates the change in the composition of hydrocarbons in sediments. Many researchers consider this relationship as an indicator of biodegradation of oil pollution - the higher its value is for the more intense the course of biodegradation [9, 13, 17–19]. In some studies, this ratio is used to identify the degree of “aging” and weathering of oil and oil products [20, 21]. An increase in this indicator from 1.46 in 2007 to 3.66 in 2015 indicates the biodegradation of oil hydrocarbons in bottom sediments. Detected in the samples of 2017 a decrease in this indicator to the value of 1.47, usually is inherent a natural geochemical background, this can indicate an attenuation of the biodegradation process, the composition of the CB samples becomes close to the natural background.

It is noted that according to our data, CPI has value > 1 in the composition of hydrocarbons of uncontaminated samples of bottom sediment (characterizing the geochemical background) as well as of native organic matter of soil samples. Both characterize a significant predominance of high molecular weight n-alkanes of composition C_{27}–C_{31} with odd number carbon atoms. Thus, the individual composition of n-alkanes of bottom sediments is quite close to the native organic matter of soil samples due to the impact of organic matter of higher ground plants. This is indicated by both the features of n-alkanes composition with a predominance of odd homologues C_{27}–C_{31} and the group components and structural-group composition of bottom samples of 2017. Our conclusion about the predominance of odd homologs in the composition of high molecular n-alkanes indicates a significant impact lipid components of higher plants to the composition of organic matter of bottom sediments of the lakes is confirmed by a number of works [3, 4, 22, 23].

4. Conclusion

Thus, the monitoring studies of 2006–2017 on the state of bottom sediments of the water area of the lake contaminated during the accidental oil spill, according to the obtained results showed that oil pollution had significantly transformed over 10 years from 2006 to 2015. It indicates by a decrease in the level of pollution as directed changes in chemical composition of oil pollution. By 2017, in the absence of new oil spills, the chemical composition of bottom sediments became to state, inherent to the native organic matter of bottom sediments of the coastal lake facies, which is characterized by the presence of compounds typical for higher plant lipids (dominance of high molecular weight n-alkanes of composition nC_{23}–nC_{33} with a significant predominance of odd homologues, a high content of oxygen-containing compounds - solid saturated fatty acids, aliphatic esters and saturated ketones).
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