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Control of Biological Treatment of Disturbed Lands of Cryolithozone at Oil Spills

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Abstract. The paper presents the results of geochemical research on the effectiveness of biological treatment of oil-contaminated permafrost soils in the conditions of the Far North (Republic Sakha (Yakutia)). On base of the complex of physics-chemical methods analysis, the comparison study of transformation features of oil contamination was made at the experimental site with application of biological preparation on the base of native strains of hydrocarbon-oxidizing microorganisms and at the control site without application of preparation. At the experimental site over 10 years' monitoring the significant changes were observed such as a content of residual oil content as in composition of oil contamination. A content of resins and asphaltene increased as hydrocarbons decreased, in the chemical structure the amount of oxygen groups and bonds increased. Degree of destruction averaged 95%. At the same time, the level of pollution remained high. Thus, a single treatment of soils with biological preparation wasn't enough to completely remediate soils. At the control site, the same direction of changes was observed with a lower rate of degradation. Degree of destruction was only 35%. Obtained positive results can be used for remediation works in territories contaminated by spills of oil and oil products.

1. Introduction

The problem of land remediation in the conditions of a cryolithozona is relevant in connection with the intensive development of oil and gas fields in the Republic Sakha (Yakutia), which is inevitably followed by contamination of soils. In soils of a cryolithozona, unlike regions with favorable climatic conditions, processes of biodegradation spilled oil and oil products proceed much more slowly that predetermines lower ability of permafrost soils to self-remediation [1, 2]. If in regions with favorable climatic conditions process of self-remediation of the oil contaminated soils without application of additional measures for remediation of the disturbed lands proceeds 10-25 years, then in the conditions of the North destruction of oil and its derivatives can last more than 50 years [3-7]. According to the analysis as literary data as results of own researches the biological method treatment of the contaminated soils by biological products on the basis of aborigine hydrocarbons oxidizing microorganisms (HOM) in the conditions of a cryolithozona is the most ecologic and effective among of the existing methods of remediation of the oil contaminated soils [8-12].

Study of processes of remediation of the permafrost soils contaminated by oil in result of the emergency spill in the territory of Lensky District of the Sakha (Yakutia) Republic was the purpose of this work. For this purpose, the experiment on biological remediation of soils contaminated by oil at the experiment site with application of a biological product into the soil was made. Comparison study



of features of processes of transformation of oil at the experimental site with treatment by a biological product on the basis of native HOM allocated from permafrost soils and at control - in the process of self-remediation of soils due to natural biodegradation is made.

2. Data and Methods

Monitoring of the contaminated territory was carried out since 2006 within 10 years at two experimental sites. In summertime at the experimental site the soils were treated by a biological product, the control site wasn't treated. In an experiment the biological preparation developed at Institute on the basis of HOM allocated from permafrost soils which were capable to develop at low positive temperatures (from +4 °C) in the conditions of low aeration, humidity and weak microbiologic activity of permafrost soils of a cryolithozone [12] had been used.

In a number of papers it is shown that researches with application of a complex of analytical methods are necessary for correct assessment of efficiency of remediation works. It allows to reveal the directed changes in structure of oil contamination demonstrating processes of degradation of oil in the soil [5]. It is possible to reveal reduction of concentration of oil with simultaneous reduction of hydrocarbons content, increase resins and asphaltenes, redistribution of hydrocarbons as of alkane and aromatic and change in chemical structure of extracts [12-18]

In this work a complex of physical and chemical methods was used. The content of oil in soils was determined by method of cold chloroform extraction by the yield of the chloroform extract. Composition of extracts was studied with use of methods of infrared spectroscopy, the liquid and adsorptive chromatography and chromatomass-spectrometry (GC/MS). IR spectra recorded on the IR-Fourier spectrometer of Protege 460 of Nicolet. The liquid and adsorptive chromatography used for fractional division of soil extracts into hydrocarbons, resins and asphaltenes components [19].

The hydrocarbon fraction studied by GC/MS. Researches were conducted on the system which is turning on the gas Agilent 6890 chromatograph having the interface with the highly effective mass and selective detector Agilent 5973N. The chromatograph is supplied with a quartz capillary column 30 m long, with a diameter of 0.25 mm, an impregnated phase of HP-5MS. Gas carrier was served helium with a speed of stream of 1 ml/min. Temperature of the evaporator is 320 °C. Programming of rise in temperature was carried out by from 100 to 300 °C with a speed of 6 °C min⁻¹. The ionizing tension of a source of 70 eV. In more detail techniques of researches are given in work [20, 21].

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

The received results showed a non-uniform character of oil contamination distribution. At the studied sites in 2006 the initial content of oil in soils varied from 156 g kg⁻¹ to 386 g kg⁻¹ that corresponded to the high level of contamination [22]. During 10 years' monitoring, the main tendency to decrease in level of contamination on both sites was observed. Nevertheless it's need to note that in separate years at the control site fluctuations in the content of residual oil were detected as in lower as in the upper direction (table 1). At the same time, level of contamination after the 10 years' monitoring remained very high (more than 10 g kg⁻¹) at both sites. More significant dynamic of decrease in content of oil was observed at the experimental site in comparison with the control (table 1).

By results of study, directed changes in chemical structure of extracts are detected. During monitoring (from 2006 to 2015) in samples from the experiment site in comparison with initial oil contamination there were a reduction of hydrocarbons (methylene and methyl groups) and increase oxygen groups and bonds (figure 1). In figures 2 and 3 a clear-cut dynamic of increase in values of relative coefficients of absorption of carbonyl groups (K_{1700}) and ester bonds (K_{1170}) is shown. It allowed making conclusion that biodegradation processes of oil contamination in soils occurred. In the spectrum of the sample from the control site (2015) absorption bands of oxygen groups and bonds with lower intensity, than in the experiment appeared (figure 1). It demonstrates that processes of

destruction of oil in the conditions of a cryolithozone at self-remediation of soils without biological remediation proceed much more slowly.

Table 1. Characteristic of oil contamination of soils samples.

Parameters	Years of monitoring							K ^a _{destr.} , %
	2006	2007	2008	2009	2011	2014	2015	
Content of oil (g kg ⁻¹)								
Control	386	167	152	131	87	185	253	34.5
Experiment	156	42	22	17	15	11	9	94.2
Group component composition of the extracts								
Hydrocarbons, %								
Control	75.4	70.6	70.3	69.8	63.9	59.4	52.0	
Experiment	74.9	51.2	45.4	28.3	22.3	19.7	21.9	
Resins, %								
Control	23.3	28.0	28.3	29.8	34.9	37.1	43.3	
Experiment	23.8	46.2	51.8	69.2	73.6	72.6	70.0	
Asphaltenes, %								
Control	1.3	1.4	1.4	0.4	1.2	3.5	4.7	
Experiment	1.3	2.6	2.8	2.5	4.1	7.7	8.1	

^a degree of distraction

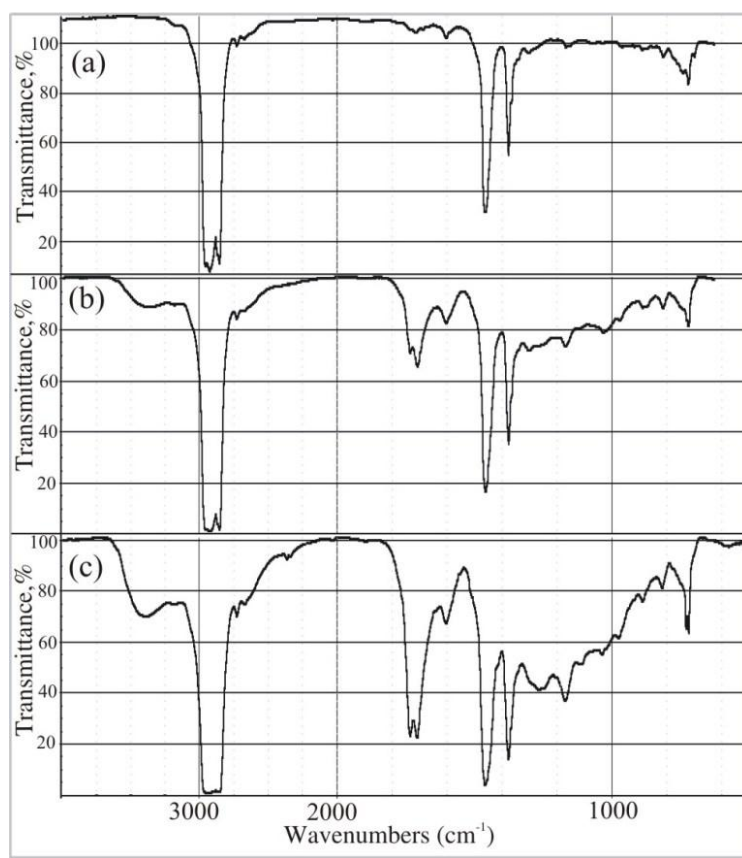


Figure 1. IR-spectra of extracts of soil samples: (a) initial, 2006; (b) from the control site, 2015 and (c) the experiment site 2015.

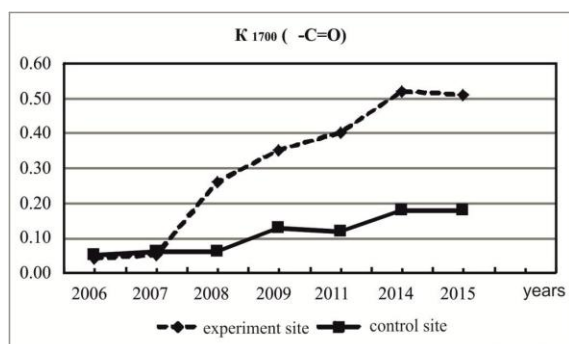


Figure 2. Increase of relative coefficient of absorption of carbonyl groups.

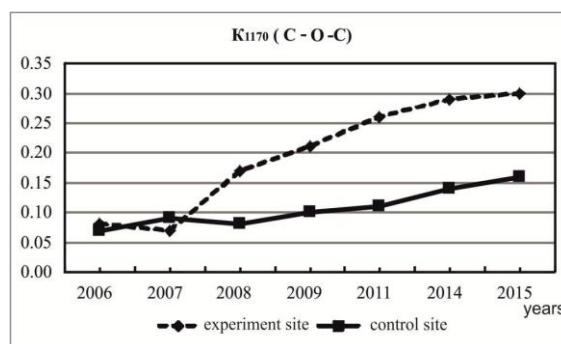


Figure 3. Increase of relative coefficient of absorption of ester groups.

The received results have shown that when using a biological product along with decrease of amount of residual oil in the soil and changes in chemical structure also the group components composition of extracts has changed. In the initial samples of 2006 from both sites hydrocarbons dominate (table 1). In the samples from the experimental site the content of hydrocarbons components has decreased by 3.5 times and has increased resins and asphaltenes in comparison with the control where the amount of hydrocarbons has decreased by only 1.5 times (table 1). It indicates that in the process of biological remediation with microorganisms, a hydrocarbon part of contamination has been utilized at first. At the experimental site in 10 years the composition of residual contamination has become a resin-asphaltene character.

According to GC/MS, considerable changes in structure and the character of distribution of individual saturated hydrocarbons of oil contamination at the experimental site are found. For the considered observation period at this site in comparison with the initial oil contamination there was an increase content of relatively high-molecular n-alkanes, the maximum distribution had moved to the high-molecular region from $nC_{15,17}$ in 2006 to $nC_{27,29,31}$ in 2015 (figure 4). The prevalence of homologs with odd number of carbon atoms in a molecule in composition of n-alkanes is detected. The values of coefficient of CPI (odd/even) are equal: 1.66-3.56 in comparison with initial oil contamination 1.07. It is known that the CPI value close to 1 is characteristic for oil. Pristan (Pr) and phytan (Ph) prevail over nearby eluted n-alkanes. The ratio $(Pr+Ph)/(nC_{17}+nC_{18})$ has considerably increased of 0.96 product in 2006 till 3.75 in 2015. Many researchers consider these ratios as oil biodegradation indicators. The higher values, the more intensively there was a rate of biodegradation processes [23]. At the experimental site the specific changes in composition of oil contamination reflect the processes of biodegradation of hydrocarbon components. A change in composition of oil contamination in the direction of approach to a natural background of soils had due to these processes. Unlike the experimental, at the control site the remarkable changes didn't notice in the character of distribution of saturated hydrocarbons among which relatively low-molecular n-alkanes with a maximum on $nC_{15,17}$ prevail throughout the entire period of monitoring. Also increase in CPI (figure 5) was insignificant.

Thus, the results of carrying out experimental works on biological remediation of the oil contaminated permafrost soils with use of the biological preparation made on the basis aborigine HOM revealed the directed changes in composition of the oil contamination. They are reduction of quantity of methyl groups and methylene chains in chemical structure of extracts and increase oxygen groups and bonds, reduction of hydrocarbon components content and increase resins and asphaltenes. It indicates that reduction of residual content of oil has been caused not only to physical and chemical processes of destruction, decontamination, dissolution, ultra-violet destruction, but also due processes of biodegradation of oil components in soils which activity has considerably increased in result of participation of the applied HOM. In general, extent of destruction at the experimental site during 10 years' monitoring had increased up to 94%.

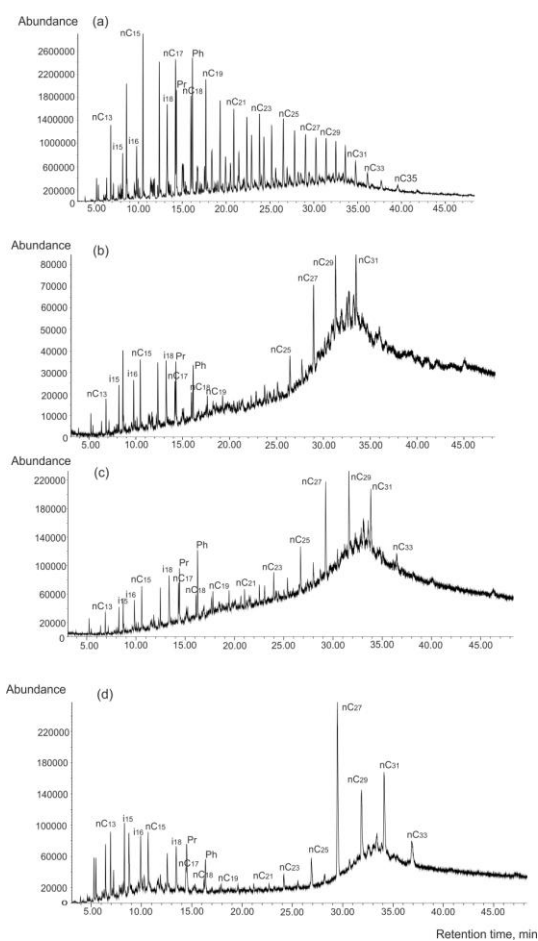


Figure 4. Mass-fragmentograms of saturated hydrocarbons in soil extracts of samples from the experiment site, taken in different years (a) 2006; (b) 2009; (c) 2011 and (d) 2015.

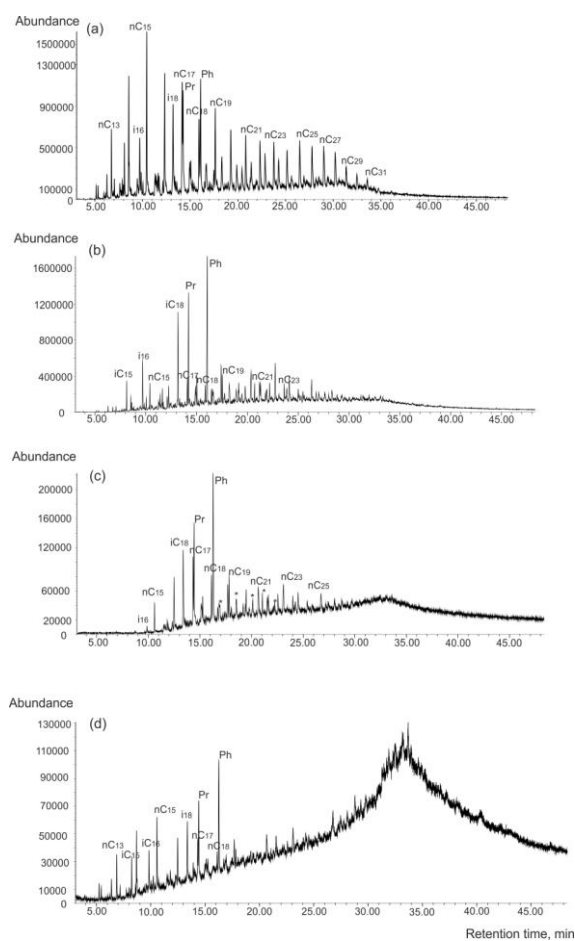


Figure 5. Mass-fragmentograms of saturated hydrocarbons in soil extracts of samples from the control site, taken in different years (a) 2006; (b) 2009; (c) 2011 and (d) 2015.

At the control site, residual oil contamination has steady character extent of destruction of oil for the same period has made only 34.5%. The composition of oil contamination has changed less considerably that indicates the low rate of self-remediation of permafrost soils generally due to physical and chemical processes as permafrost soils of a cryolithozone are characterized by weak microbiological activity [3, 24, 25].

4. Conclusion

Thus, results of comparison study have shown that HOM applied into the soil with a biological preparation, sharply intensified biodegradation processes of oil contamination. By our estimates, in addition due to introduction of a biological preparation about 60% of oil has been utilized by microorganisms. The received results show high efficiency of biological remediation of the oil contaminated soils when treatment by the biological preparation developed at Institute on the base of HOM allocated from permafrost soils which are capable to develop and keep activity at low positive temperatures. The positive experience can be used in territories of various objects of oil and gas complex when carrying out works on remediation of the oil contaminated permafrost soils of a cryolithozone.

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