Experience in the Remediation of Oil Polluted Soils of the Arctic Zone of Yakutia

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Abstract. In the Arctic zone of Yakutia, geochemical studies have been carried out to study the state of the soil in one of the tank farms. The row of informative analytical indicators was used to characterize the composition of oil pollution and assess the features of its biodegradation processes in permafrost soils. The features of the chemical composition of oil pollution in soil samples with a long-term contamination are revealed and are taken into account at developing methods for cleaning soils from "old" oil pollution. An experiment on the biological treatment of soils with a biological product based on indigenous hydrocarbon-oxidizing microorganisms isolated from permafrost soils was conducted. The initial oil content was 34594 mg kg⁻¹. After 3 months of incubation of a biological product, along with a decrease in the residual oil content, the composition of pollution changed in the direction of increasing the content of resin-asphaltene components and decreasing hydrocarbons. The proportion of oxygen-containing groups and bonds has significantly increased in the chemical structure of alcohol-benzene resin. In the composition of alkane hydrocarbons, a redistribution is established both within the homologous series and between different rows of homologues. The degree of destruction of oil pollution reached 56.6%

1. Introduction
International experience in mitigation measures shows that in the Arctic, only 10 – 15% of oil can be collected and eliminated due to the harsh climatic conditions, the lack of a developed infrastructure and the remoteness of the search and rescue services [1, 2]. The transportation of oil and oil products is the most dangerous of oil pollution [1, 3, 4]. Experience shows that the development of the resources of the Arctic shelf should be accompanied by advanced study of the ecological status of the coastal shelf zone, identification of "hot" spots – the places with a high level of oil pollution and the development of effective and environmentally friendly ways to restore disturbed lands [1].

For the seas of the Eastern Arctic the main contribution to the total contribution of petroleum hydrocarbons is made by river flows [1, 4, 5, 6]. In Yakutia, oil and petroleum products are delivered to the Arctic regions along rivers, bulk plants are along their banks. Transportation of oil and oil refineries and the operation of bulk plants accompanies by the risk of pollution of water and the coastal land [7]. In this conditions residual oil pollution persists for many years and initially local pollution can spread over large areas [1, 9, 10]. The territories where the objects of distribution and storage of oil and petroleum products are located belong to the category of territories with high technogenic load.
The main sources of pollution are systematic leaks and spills during the intake, storage and release of petroleum products. The territories of tank farm, as a rule, are characterized by large variations in the level of pollution and unimform distribution, due to the nature of chronic and accidental leaks of petroleum products, different in scale, composition, intensity, timing of occurrence and duration.

This paper presents the results of a geochemical study of soil conditions at the place of the tank farm with a long period of contamination and the experience of its biological treatment. The obtained data will be useful to identify the main factors affecting the characteristics of the processes of transformation of petroleum hydrocarbons in permafrost soils, its speed and direction [11, 12, 13]. The results will have of practical importance for the development of optimal methods for the remediation of technogenic-disturbed areas, the choice of methods of cleaning and, as a consequence, reducing the cost of its implementation [12, 14].

2. Data and methods

The object of the study was the territory of the tank farm, located on the banks of the Kolyma River, in the Arctic zone of the Republic of Sakha (Yakutia, the Nizhnekolymsky district). The studies were carried out in order to identity a composition of the “old” oil contamination of soils formed due to the accumulation of petroleum products as a result of spills and leaks over the long years of operation of the tank farm. For comparison, we studied the composition of oil as an oil pollutant in the studied area of the tank farm, and the composition of a background soil sample taken at the border of the tank farm at a large distance from pollution sources.

The experiment site of a 120 m² was laid on the territory of the commodity park for the test an efficiency of biological product for the treatment of oil-contaminated soils. The term of contamination of this site is more than 10 years. The biological preparation for the experiment was developed at the Institute of Oil and Gas Problems SB RAS. It was prepared on the basis of hydrocarbon-oxidizing microorganisms isolated from permafrost soils that can develop at low positive temperatures (from +4 °C) under conditions of low aeration, humidity and weak microbiological activity of permafrost cryolithozone [15]. The initial soil samples taken before biological treatment (July 5, 2013) and samples taken 3 months after cleaning (September 25, 2013) were the material for research.

The row of researchers believe that studies with application of a complex of analytical methods are necessary for a correct assessment of efficiency of clearing works. This makes possible to identify main changes and its direction in the composition of oil pollution, indicating the processes of oil degradation in the soil [7, 9, 12, 15, 16, 17]. These changes include a decrease in the concentration of oil with a simultaneous decrease in the proportion of hydrocarbon and an increase in resins and asphaltenes, the redistribution of hydrocarbons in the composition of alkanes and arenes and changes in the chemical structure of extracts [9, 15, 17, 18, 19].

In this work 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 adsortive 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, resines and asphaltenes components.

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⁻¹. 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 [11].

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 content of the chloroform extract in the background soil sample was 348 mg kg⁻¹. There are some differences in composition of this sample in comparison with typical background samples from areas of natural objects. They are some increase of hydrocarbon components (51% compared to 4 - 20% in pure soils in the group composition of the soil extract, appearance in the spectrum of absorption bands (a.b.) of aromatic hydrocarbons - 750, 810 and 1600 cm⁻¹, which can be considered as traces of oil pollution (Figure 1 c). A similar composition is typical for background soil samples at technogenic objects, such as tank farm [9, 20].

The initial oil content in the combined sample from the test site was 34594 mg kg⁻¹, it corresponded to a high level of pollution [21]. This area was intensively impregnated with viscous oil as a result of the spill that had occurred more than 10 years ago. The soil sample characterized as "old" oil pollution, which had was underwent to deep degradation. This indicated by the IR spectroscopy data on the presence of intense absorption of carbonyl and hydroxyl groups - 1700 and 3300 cm⁻¹ and aromatic compounds – 810 and 1600 cm⁻¹ oil (Figure 1 b) in contrast to the IR spectrum of oil sample. As can see (Figure 1, a) the IR spectrum of oil sample is exclusively characterized by a.b. hydrocarbon structures (methylene and methyl groups, aromatic rings). Thus, by the nature the sample spectrum with "old" pollution has a great similarity with the spectra of polluted samples of soil undergone to deep degradation.

The data on group composition also give certain information about the term of soil pollution. In the initial soil sample characterized by a long time period after oil spill and transformation of pollution, the amount of hydrocarbons was only 65%, at the same time, the content of resins and asphaltene components was 35%, which wasn’t typical for composition of oil pollutants with inherent hydrocarbons domination (Table 1).

In contrast to the "old" pollution, the characteristics of pollution of “fresh” oil spills correspond to the characteristics of the pollutant, in this case oil sample [22]. Group composition is characterised by a predominance of hydrocarbons (70-88%) over the resinous components and asphaltenes [11]. These two types of pollution also differ by distribution of alkane hydrocarbons, as indicated by the differences in proportions: the isoprenoids/n-alkanes, relatively low molecular weight n-alkanes to high molecular weight alkanes (Σn-C_{1b.b.-20}/Σn-C_{21-c.b.}), pristane (Pr) over heptadecane (n-C_{17}), phitan (Ph) over octadecane (n-C_{18}) [11, 23].

The ratio of normal alkanes to isoalkanes is determined by the degree of "aging" and weathering of oil pollution, during which at first the n-alkanes are underwent to biodegradation [9, 10, 12]. In the initial "old" pollution an increase in the ratio of Pr/n-C_{17}, Ph/n-C_{18} was found, which indicated the processes of biodegradation of oil pollution in time (Table 1, Figure 2 a).

The detected differences of the chemical composition of soil samples in the direction of reducing the role of oil hydrocarbons, the changing of their distribution and increase of oxygen-containing compounds confirmed that a lot of time had passed from the moment of oil spill. As can see the composition of oil pollution had changed due to slow processes of degradation in the cryolithozone conditions but a level of pollution stayed rather high. In the works of the Russian and foreign scientists in the Arctic regions, it has shown that oil pollution is capable will stay for many years in such conditions [8, 9, 10, 17]. In the Arctic, temperature regime, level of occurrence of permafrost, content of organic matter content in soils, soil biological activity, aeration conditions are the main factors which effect on transformation of oil hydrocarbons [9, 16]. According to our data, after the accident on the oil pipeline in the middle taiga zona of Yakutia the degree of degradation of oil pollution along 10 years was about 50 % without carrying out actions for cleaning of soils. At the same time, the level of pollution stayed quite high. The feature of distribution of individual hydrocarbons and the structural-group composition of soil extracts as a whole were far from characteristics of background soils [10].
Figure 1. IR-spectra of samples: oil (a), soil extract with the initial "old" oil pollution (b) and background soil (c).

Figure 2. Chromatograms TIC of saturated hydrocarbons: initial "old" pollution (a), 3 months after treatment (b).

Table 1. Geochemical characteristic of the samples composition.

| Parameters | Pollutant (oil sample) | Initial "old" pollution | 3 months after treatment |
|------------|------------------------|--------------------------|-------------------------|
| Oil content, mg g⁻¹ | 34594 | 15015 |
| **Group component composition, %:** | | | |
| Hydrocarbons | 87.0 | 64.9 | 50.5 |
| Benzo resins | 6.0 | 5.5 | 14.5 |
| Alcohol-benzol resins | 6.4 | 10.4 | 14.3 |
| ∑resins | 12.4 | 15.9 | 28.8 |
| Asphaltenes | 0.5 | 19.2 | 20.6 |
| **The relative absorption coefficients of alcohol-benzene resins:** | | | |
| Carbonyl groups $D_{1700}/D_{1460}$ | 0.21 | 0.80 | 2.08 |
| $D_{1700}/D_{1600}$ | 0.82 | 2.34 | 3.35 |
| Ether bond $D_{1170}/D_{1260}$ | - | 0.41 | 0.71 |

| Individual composition alkane hydrocarbons: | | | |
| $\sum_{b.b.t.} nC_{30}/\sum_{e.b.t.} nC_{21}$ | 5.21 | 4.74 | 1.93 |
| Isoprenoids/n-alkanes | 0.33 | 0.92 | 2.56 |
| Pr/n-C₁₇ | 0.45 | 1.95 | 4.39 |
| Ph/n-C₁₈ | 0.91 | 1.98 | 3.76 |
| Pr+Ph/n-C₁₇+ n-C₁₈ | 0.63 | 1.96 | 4.04 |

a $D_{1460}$ - optical density of the absorption of long methylene chains
b $D_{1600}$ - optical density of the absorption of aromatic cycles
c b.b.t. temperature of beginning boiling; e.b.t. temperature of end boiling
In the experiment on the biological treatment of soils with “old” pollution, it is possible to exclude the influence of physical factors on changes in the composition of oil pollution, because these processes usually occur in the first years after the oil spill [12]. Therefore, in our experiment, we consider the destruction process of oil pollution as result of the biological preparation action. During the 3 months of incubation of the biological product in the soil, the residual oil content decreased, the degree of destruction reached 56.6% (Table 1). Changes in the composition of the pollution, namely, increase of content of resinous-asphaltene components and decrease hydrocarbons compared with the original pollution have shown (Table 1). The data of the structural group composition of alcohol-benzene resins of the studied samples, namely the relative absorption coefficients of oxygen-containing groups and bonds indicate the direction of the processes of microbiological destruction most clearly. After 3 months, the absorption coefficients of carbonyl groups D_{1700}/D_{1600} increased 2.6 times and D_{1700}/D_{1600} 1.5 times as ether groups and bonds D_{1170}/D_{1460} increased 1.7 times (Table 1).

The composition alkane hydrocarbons changed as shown the redistribution of their homologues. As a result the content of n-alkanes decreased, and content relatively low-molecular homologues also decreased in their composition (Table 1, Figure 2 b). The isoprenoid content increased 1.3 times according to the ratio of isoprenoids to n-alkanes. The ratio of (Pr+Ph)/(n-C_{17} + n-C_{18}) increased 2 times (table 1). Many researchers this ratio use as a coefficient of microbial degradation [9, 10, 14, 24]. The coefficient increase in the row: oil (as a pollutant) → initial "old" pollution → changed oil pollution after 3 months of bioincubation indicated the destruction of the least resistant to biodegradation of n-alkanes C_{17} and C_{18} and the relative accumulation of more stable isoprenoids Pr and Ph [9].

4. Conclusion
In the Arctic zone of Yakutia during detailed study the features of the chemical composition of oil pollutions soils with different term are established by a row of analytical parameters.

The degree of destruction of pollution reached 56.6% in the experience of treatment of permafrost soils of “old” oil pollution with a biological product developed at the Institute of Oil and Gas Problems SB RAS.

The results allow us to consider the use of biological treatment as one of the effective approaches for remediation soils in the Arctic. However, the results of the experiment showed that a single treatment with a biological product in the Arctic was not enough for the complete remediation of disturbed soils, since the residual level of pollution stayed high enough and was 15015 mg kg\(^{-1}\).

The obtained experience in biological treatment of oil-contaminated soils on the territory of the tank farm can be useful for remediation works in other areas of the Arctic zone.

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