Features of Transformation of Oil-contaminated Soils in Arctic Region

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Abstract. A study of the comparative characteristic of Yakutia’s frozen soils ability to remediation, when contaminated with oil, has been carried out. The samples of permafrost soils from the territories of the the Republic of Sakha (Yakutia), exposed to industrial pollution by oil and its products, with old periods of pollution (10 ÷ 12 years) were examined. Remediation was not carried out anywhere. In the soils of the western part of Yakutia, despite a high residual level of pollution (8.58%), signs of oxidative destruction of petroleum hydrocarbons are clearly visible (high content of resinous components (61.3%)), and almost complete transformation of acyclic hydrocarbons. In arctic soils, self-remediation processes occur at a significantly slower pace. In these soils the content of hydrocarbon fractions is still high (60.3-64.9%). There is no selectivity in the transformation processes of individual acyclic hydrocarbons. This suggests that the oxidative destruction of oil pollution in Arctic soils is mainly influenced by physical and chemical environmental factors, rather than microbiological oxidation. The low microbiological activity of hydrocarbon-oxidizing microorganisms in the Arctic soils indicates the need to develop special remediation measures to clean the soil from oil pollution.

1. Introduction

The anticipated intensive development of the Arctic region is primarily associated with the hydrocarbon production. It is known that 2-3% of world oil production is lost due to spills, leaks, and other sorts of accidents [1]. It can be assumed that under the conditions of the Arctic, the magnitude of the losses will be even higher, since due to its extremely low temperatures, the probability of emergency situations sharply increases [2]. Oil and petroleum products are dangerous sources of environmental pollution; as well as their transformation products, which are no less toxic [3-5]. As a result, it is already necessary to develop effective ways to clean up arctic soils from oil pollution. The climatic features of the Arctic region impose their own specifics on remedial measures. According to many experts, only biological methods are suitable for the remediation of arctic soils from oil pollution [6-9]. Only those allow minimal damage to the fragile northern biocenoses. The importance of timely measures to eliminate oil pollution is also connected to the problems of permafrost degradation. Destruction of vegetation covers in arctic conditions lead to the permafrost thawing, waterlogging, and greenhouse gas emissions into the atmosphere [10].

The purpose of this work was to study the ability of the Arctic soils to remediation when contaminated with oil. Earlier, we considered the self-remediation dynamics of the cryolithozone soils...
in the western part of Yakutia using the example of the territory of the former Talakan-Vitim oil pipeline [11]. 12 years have passed since the large-scale accident on the oil pipeline, however, the level of oil pollution is still very high and reaches 23.50 ± 29.40% in some sections. Nevertheless, in the composition of oil pollution, the characteristic features of the oxidative degradation of petroleum hydrocarbons are clearly visible. In the Arctic region, the climatic conditions are even more severe, the frozen layer is closer to the day surface of the earth, the soil cover is thin, and poorly developed [12]. All this may further slowdown the rate of soil recovery from oil and petroleum product spills. Work on the environmental safety of the Arctic region from hydrocarbon pollution was carried out by individual researchers [13–16]. The development of effective biological methods for the recovery of arctic soils includes the need to study the self-remediation capacity of these soils.

2. Experimental part

2.1. Objects and research methods

For the research in the Arctic zone, areas with a long-term contamination were selected on the territory of the Nizhny Kolymskaya tank farm and the Nizhnye Kresty tank farm near the village of Petushki. For comparison, studies were also conducted on one of the sites of the former Talakan-Vitim oil pipeline (Western part of Yakutia). In all cases, the duration of oil pollution took place for approximately 10–12 years. No remediation work was carried out at any of the sites, and new spills were not recorded. The Nizhny Kolymsky tank farm is operative. Given the ability of oil pollution to migrate [11, 17, 18], in the event of new spills in other areas of the tank farm, re-contamination of the studied area may occur. Nizhnye Kresty tank farm near the village of Petushki has not been used for over 10 years. As a result, it is possible to study the ability of Arctic soils to remediation in the absence of possible distortions associated with new spills.

The objects that were examined were soil samples taken from the studied sites. They were freed from organic residues (roots, leaves), dried, triturated, sieved, and subjected to cold chloroform extraction. To determine the level of contamination of soil and bottom sediments by oil and its products, generally accepted methods have been developed [19, 20]. However, as shown by the results of our studies and other authors [8, 9, 11, 18, 21–23], these techniques are applicable only for fresh spills, since they do not take into account the contribution of asphalt-resinous components, which are products of transformation of oil pollution. As a result, the level of oil pollution was determined by the yield of chloroform extracts (ChE). To study the processes of transformation of oil pollution, the isolated ChE were studied by means of infrared spectroscopy, liquid-adsorption chromatography and chromatomass-spectrometry. Details of the sampling method and research methods are given in [11].

2.2. Results and their discussion

Table 1 shows the results of the analytical studies. It can be seen that the level of oil pollution in the area of the former Talakan-Vitim oil pipeline is almost two times higher than in areas from the Nizhny Kolymsky tank farm. However, in the compositions of ChE, the content of hydrocarbons in the Arctic samples is significantly higher than in the soil from the territory of the pipeline. The processes of transformation of oil pollution associated with oxidative destruction of hydrocarbons under the influence of physico-chemical environmental factors and biodegradation by hydrocarbon-oxidizing microorganisms, usually present in the soil. The high content of hydrocarbon fractions in the ChE of arctic samples indicates a sluggish current process of oxidative degradation of hydrocarbon components of oil pollution.

This is also indicated by the nature of the IR spectra of the ChE of the samples ‘figure 1’. It can be seen that the components of oil pollution in a soil sample from the territory of the pipeline are much more oxidized than those from the territories of Arctic tank farms. This is evidenced by a higher absorption in the region of oxygen-containing groups: absorption band (a.b.) 3300-3400 cm⁻¹, characteristic of hydroxyl groups, a.b. 1700 cm⁻¹ - for carbonyl groups and a.b. 1170 cm⁻¹ - for ether bonds. In the IR spectra of the ChE of the arctic soil samples, there is a higher absorption of the
methyl and methylene groups (a.b. 1460 cm\(^{-1}\)), as well as aromatic structures (points 750, 810, 1600 cm\(^{-1}\)) which are characteristic of petroleum hydrocarbons.

**Table 1.** Yield and group composition of chloroform extracts.

| Place of selection                  | Yield of ChE, % | Group composition of chloroform extracts, % |
|-------------------------------------|----------------|------------------------------------------|
|                                     |                | Hydrocarbons, % | Resins, % | Asphaltenes, % |
| Nizhny Kolymskaya tank farm         | 3.459±0.00     | 64.9±3.2       | 15.9±0.8  | 19.2±0.9       |
| Nizhnye Kresty tank farm            | 4.815±0.00     | 60.3±3.0       | 29.3±0.2  | 10.4±0.5       |
| Former Talakan-Vitim oil pipeline   | 8.581±0.00     | 34.7±1.7       | 61.3±0.3  | 5.0±0.3        |

Reliability of arithmetic mean values in comparison with control and background: \( p \leq 0.05, t > 3 \)

**Figure 1.** IR spectra of chloroform extracts of soil samples: a – Nizhny Kolymskaya tank farm; b - Nizhnye Kresty tank farm; c - former Talakan-Vitim oil pipeline.
To study the processes of biodegradation of oil pollution, the hydrocarbon fractions of ChE were studied by using the method of gas chromatography / mass spectrometry ‘figure 2’. It is known that normal alkanes, including \( \text{nC}_{17} \), \( \text{nC}_{18} \), and only the last isoprenoids are subjected to biodegradation [24, 25]. As a result, the ratio of the sum of isoprenoids of pristane and phytane to the sum of the next eluting n-alkanes \( \text{n-C}_{17} \) and \( \text{n-C}_{18} \) (\( \sum \text{Pr} + \text{Ph} / \sum \text{nC}_{17} + \text{nC}_{18} \)) can be used to evaluate the intensity of the processes of biodegradation of oil pollution. It can be seen ‘figure 2 (c)’ that in the soil selected from the territory of the former Talakan-Vitim pipeline, almost all hydrocarbons underwent transformation processes. In the composition of the hydrocarbon fraction, not only n-alkanes were absent, which are primarily utilized by hydrocarbon-oxidizing microorganisms, but also isoprenoids, the most resistant to the effects of microorganisms.

**Figure 2.** Mass chromatograms of hydrocarbon fractions of ChE soil samples: a – Nizhny Kolymskaya tank farm; b - Nizhnye Kresty tank farm; c - former Talakan-Vitim oil pipeline.
It should be noted that we have been monitoring the territory of the Talakan-Vitim pipeline since 2006, immediately after a large-scale accident. 2-3 years after the accident, selectivity in the transformation of acyclic hydrocarbons began to show clearly in the distribution of individual hydrocarbons. The coefficient $\Sigma Pr + Ph / \Sigma nC_{17} + nC_{18}$ after 6 years since the accident reached a value of 6.9 [11]. However, 12 years after the accident, as can be seen in ‘figure 2’, there are practically no normal alkanes or isoprenoids in the hydrocarbon fraction. The mass chromatogram of this sample is characterized by the presence of a “hump”, which is caused by a high content of high-molecular, undivided methane-naphthenic and naphthenic-aromatic hydrocarbons [24], probably intermediate products of the transformation of petroleum hydrocarbons. In the hydrocarbon fractions of ChE in Arctic samples ‘figure 2 (a, b)’, the distribution of individual acyclic hydrocarbons in contaminated samples is close to that of oil, the ratio $\Sigma Pr + Ph / \Sigma nC_{17} + nC_{18}$ is low and equal to 1.9 and 1.4 respectively. According to the assessment of the intensity of microbiological oxidation processes, this pollution is characterized as slightly affected by biodegradation processes. It should be noted that the mass chromatogram of soil samples from the Nizhny Kresty tank farm ‘figure 2 (b)’ is also characterized by the presence of a “hump.” That is, the hydrocarbons transformation processes occurred in this area. On the oxidative degradation of oil pollution indicates, as noted above, the nature of the IR spectrum of this sample ‘figure 1 (b)’. However, there is practically no selectivity in the transformation of acyclic hydrocarbons inherent in microbiological oxidation. As a result, we can assume that in the Arctic sample from the Nizhny Kresty tank farm, the oxidative destruction of hydrocarbons predominantly proceeded under the influence of physicochemical environmental factors, and not those of microbiological oxidation. On the mass chromatogram from the Nizhny Kolymsky tank farm such a "hump" is absent. Apparently, in this case, the flow of hydrocarbons caused by fresh spills cannot be excluded, since this tank farm is operational.

3. Conclusion
To study the ability of permafrost soils in Yakutia to remediation, soil samples were studied from areas of Arctic tank farms: Nizhny Kolymskaya and Nizhny Kresty, as well as from the territory of the former Talakan-Vitim oil pipeline (Western Yakutia). All sites are characterized by a long-term period of oil pollution (10 ÷ 12 years) and remediation measures were not carried out. It is shown that in the soil from the pipeline, despite the high residual level of pollution (8.58%), signs of oxidative degradation of hydrocarbon components of oil are clearly visible. The transformation of oil pollution proceeded under the influence of physicochemical factors and microbiological oxidation. In soil samples from arctic tank farms with a significantly lower level of pollution (3.46% and 4.82%), signs of oxidative degradation are less pronounced. According to the mass spectrometry data in the Arctic soils, there is practically no selectivity in the transformation processes of individual acyclic petroleum hydrocarbons. This suggests that the oxidative destruction of oil pollution in these soils predominantly proceeded under the influence of physicochemical environmental factors, and not microbiological oxidation.

Thus, in spite of the fact that all the soils were taken from oil-polluted areas characterized by the presence of a cryolithozone, the dynamics of their self-remediation differs. In the Arctic, compared to the Western part of Yakutia, the processes of oxidative degradation of oil pollution proceed more slowly. Low rates of remediation of contaminated with oil and oil products soils have been noted by researchers in other northern regions [7, 14, 25, 26]. All this contributes to the fact that there is a need to develop special remediation measures to clean Arctic soils from oil pollution.

References
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