Features of the Petroleum Hydrocarbons Destruction in the Soils of Objects of the Fuel and Energy Complex of Yakutia

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Abstract. The paper presents the data on 8-year monitoring of the remediation of disturbed lands and the assessment of the effectiveness of biological treatment of oil-polluted soils. The positive effect of the clean-up work was clearly seen annually for only one summer season. An increase in the level of pollution by the beginning of each next season was most likely due to the oil migration from the underlying soil horizons to the near-surface ones. The data obtained on the chemical composition of the soil samples taken from a depth of up to 100 cm showed that oil content was 2 times higher than on the surface. With depth increasing the amount of hydrocarbon components had become more in the composition of soil extracts, while the content of resins and asphaltenes had decreased. This could mitigate the positive effect of reclamation work.

1. Introduction

Ensuring the sustainable functioning and restoration of ecosystems disturbed as a result of the activities of enterprises of the fuel and energy complex is a priority task of environmental protection. Despite the high requirements for minimizing pollution and the transition to the most environmentally friendly technologies for cleaning oil-contaminated soils and grounds, there is a risk of disturbance and pollution of soils with oil and oil products, which entails negative consequences for the natural environment. According to the Ministry of Ecology, Nature Management and Forestry of the Republic of Sakha (Yakutia), over the past 12 years, the number of oil and oil product spills had amounted to more than 316 cases [1]. In most cases, spills occurred during the transportation of oil products at road accidents. Spills also occurred due to the technical condition of storage tanks for oil products, non-compliance with industrial safety requirements during discharge, pumping, as well as due to weather conditions and man-made disasters (floods, fires). Significant natural resources of hydrocarbon raw materials are concentrated on the territory of Yakutia. Crude oil production in 2019 amounted to 14.1 million tonnes. [1]. It is planning to explore and include in the development of new fields, in the future as the shelf of the Arctic zone. Within the framework of the "Energy Strategy of the Republic for the Period up to 2030" it is planned to create an oil refining industry [2]. The operation of oil and gas facilities in permafrost conditions don’t eliminate risk of emergencies, sometimes including the scale of environmental disasters, such as one of the largest accidents. For example in 2020 in the city of Norilsk the leak was of more than 20 thousand tons of diesel fuel [3].

The physical, chemical and biological methods are used, as well as their combinations [4-9] for remediation soils polluted with oil and oil products. According to the principle of action, all methods can divide into artificial and intensifying natural self-purification processes. Unfortunately, such
methods of oil spill response as burning, backfilling of polluted areas with soil or sand are still used, which are unacceptable [5]. In this regard, issues related to the elimination of oil spills and the development of environmentally effective methods for restoration of disturbed lands in the permafrost zone and development of performance indicators for assessing the quality of cleaning works are actual.

2. Data and methods
The goal of this work was to assess the quality of the biological treatment of oil-polluted soils "in-situ" directly at the spill site without moving the soil ground. The object of research was the plot of territory with oil-polluted soil, where in 2010-2012 experimental work on biological treatment had been carried out. For this, a biological product had been used for cleaning oil-polluted soils. The biological product was prepared with using of aboriginal hydrocarbon-oxidizing microorganisms isolated from the soils of Yakutia [10]. Monitoring of this site was carrying out for 8 years. The soil samples were taken at the end of May and at the beginning of September each year.

In the samples there were determined a content of chloroform bitumoid (ChB) by the extraction method as the structural-group composition of ChB 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\(^{-6}\) m. The atlases of the IR-spectra and the wave number tables [11, 12] were used for the spectra interpretation. The relative absorption coefficients of carbonyl groups, ether and hydroxyl compounds, which characterize the degree of oil oxidation, were calculated by the IR-spectra of ChB. Liquid adsorption chromatography was used for the fractional separation of the soil extracts into hydrocarbon, resinous, and asphaltene resin components, and the content of methane-naphthenic and naphthenic-aromatic hydrocarbons was determined in the hydrocarbon composition [13].

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.

More detailed research methods are given in [9, 14].

3. Results and discussion
In the first year (2010) of biological remediation, 3.5 months after soil treatment with a biological product, a decrease in the concentration of oil in the soil was found, the degree of destruction was 59%. In subsequent years: 49% in 2011 and 54% in 2012. The decrease in oil concentration was consistent with the changes in the chemical composition of oil pollution. This could detect by decrease of the petroleum hydrocarbons quantity of and the increase in the proportion of oxygen-containing compounds, which indicated the biochemical oxidation of petroleum hydrocarbons.

For 8 years of this site monitoring, it had been found that almost annually by the beginning of the new season (by May of the next year), the concentration of oil in the soil increased again (Fig. 1). Thus, by May 2013, in the absence of new spills, the oil content increased 2.5 times compared to the initial one in 2010.
Figure 1. Dynamic of oil content alteration in soil.

In 2016 to find reasons for the annual fluctuations in pollution level, soil samples were taken at this site from different depths: from the surface to 100 cm. Table 1 showed that the oil content increased with depth, and the amount of hydrocarbon components in the composition of soil extracts increased. Among hydrocarbons content of methane-naphthenic (Me-Na) hydrocarbons had rose and resins and asphaltens decreased. The relative absorption coefficients of structural groups, calculated from the results of FTIR spectrometry ($D'_{720}$ - long methylene chains, $D'_{1710}$ - carbonyl groups) indicated a more oil-like character of the samples from the depth of 50-100 cm (Table 1).

Table 1. Geochemical composition of soil samples.

| Depth, cm | $C_{OP}$, mg kg$^{-1}$ | Group composition, % | HC-composition, % | Relative spectral coefficients |
|-----------|------------------------|----------------------|------------------|------------------------------|
|           |                        | Hydrocarbons | Resins+ Asphalenes | Me-Na | $D'_{720}$ | $D'_{1710}$ |
| 10        | 20990                  | 67.7        | 32.3              | 50.4  | 0.108     | 0.084     |
| 30        | 38810                  | 67.6        | 32.3              | -     | -         | -         |
| 50        | 33678                  | 76.0        | 21.0              | 54.6  | 0.123     | 0.047     |
| 80        | 43477                  | 75.7        | 24.3              | -     | 0.124     | 0.050     |
| 100       | 42917                  | 75.2        | 24.8              | 58.5  | 0.130     | 0.043     |

$C_{OP}$ – oil products concentration

When oil spreads deep into the soil layer, the processes of transformation of oil pollution are almost completely stopped, since at a depth the necessary conditions for its destruction become unfavorable: the access of oxygen, ultraviolet radiation is limited, the water-air regime of the soil is disrupted. Oil pollution retains the ability to expand the pollution area due to the intra-soil migration of oil hydrocarbons. Hydrocarbon oxidizing microorganisms are known to be most active in the upper soil layer (0–20 cm) [15–17]. The absorption coefficients of carbonyl groups were 2 times higher than in deeper soil horizon that indicated the processes of biochemical oxidation of petroleum hydrocarbons in the upper soil horizon (Table 1). At depth, petroleum hydrocarbons are not available for the action of a biological product, since the microorganisms included in its composition are capable of utilizing oil only in the aerated soil layer. Due to the lack of air oxygen and ultraviolet radiation, their activity drops significantly and biodegradation processes practically did not occur, which confirmed by the results of analysis of soil samples (Table 1). The presence of permafrost also complicated the transformation processes of oil hydrocarbons. The permafrost layer served as a physical and geochemical barrier. Experimental studies in laboratory and field experiments had shown that oil pollution spread to the depth of the seasonal thawed layer and practically did not penetrate into the permafrost layer [18-20].
4. Conclusion
The analysis of data on 8-years monitoring of oil pollution spreading along soil layers suggested a possible reason of annually oil content increase, which could be due an oil migration from more deep horizons to surface. As a result, the positive effect of biological cleaning had reduced.

Elimination of oil pollution in deeper soil layers requires the use of special cleaning technologies with ground displacement (ex situ) and soil treatment at special sites or biological products based on anaerobic bacteria.

5. References
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