The European Journal of Technical and Natural Sciences 2023, No 4–5
ISSN 2414-2352

PREMIER Publishing
ppublishing.org

Section 3. Chemistry

DOI:10.29013/EJTNS-23-4.5-17-21

METHODS OF EXTRACTING OIL CONTAMINANTS FROM ABSHERON SOIL

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Cite: *Ismailova Kamal. (2023). Methods of Extracting Oil Contaminants from Absheron Soil. European Journal of Technical and Natural Sciences 2023, No 4–5.* https://doi.org/10.29013/EJTNS-23-4.5-17-21

Abstract

The detrimental impact of heavy oil fractions is attributed to the formation of a mechanical barrier between seeds, the root system, and the surrounding environment, hindering water-air and nutrient regimes. Soil biota also experiences significant suppression. Oil-contaminated soils undergo various transformations depending on the composition and duration of pollutant exposure, leading to changes in soil structure and even the compositional makeup of oil. This study presents the results of soil samples with high concentrations of oil fractions. It is established that oil-contaminated soils undergo substantial structural changes under environmental influence, including agglomeration with the formation of long hydrocarbon chains and difficult-to-break complexes. This should be considered in the development of soil remediation methods for oil contamination. Additionally, this factor serves as a continuous source of hydrocarbon pollution in the atmosphere. A mechanism for the action of this phenomenon is proposed.

Keywords: *oil-contaminated soil, oil hydrocarbons, solvent, volatile components, chromatography*

Introduction

The oil industry is recognized as a polluter of the natural environment, causing damage to the biosphere. Specific areas, due to oil spills, approach ecological disaster zones. There is a threat of sustainable, often irreversible, transformation of natural environment components when ecosystems' normal functioning is disrupted, affecting the life processes of plants, animals, and humans. Oil pollution is accompanied by changes in the physical, chemical, and biological properties of soils. Natural soil self-purification from oil contamination can take decades. Traditional methods of restoring oil-contaminated soils (burning, burying) are not only inefficient but also environmentally harmful (Babaev, E. R., 2018).

Burning oil products affect vegetation and animal populations; pyrolysis of oil and its components results in toxic polycyclic aromatic hydrocarbons. Covering oil spots sharply reduces the speed of oil destruction, creates an unfavourable anaerobic environment, and so on. Therefore, finding environmentally and human-friendly means and methods of bioremediation for oil-contaminated soils becomes particularly relevant. Changes in soil properties due to oil pollution and the speed of oil destruction are determined not only by the pollutant dose but also significantly by the initial microbiological activity of the soil (Macaulay, B. M., & Rees, D., 2014).

Soil pollution with oil leads to a sharp change in its properties: the soil becomes hydrophobic, causing a sudden change in its agrophysical and especially hydro-physical properties (Rakhmanova, G. F., Sharonova, N. L., & Degtyareva, I. A., 2016). The carbon-to-nitrogen ratio is severely disrupted, and the content of plant-available nutrients (nitrate nitrogen, mobile phosphorus, exchangeable potassium) decreases. These changes, along with the direct toxic impact of pollutants on plants, are the cause of death and reduced productivity of agricultural crops on contaminated soils. Light fractions of oil, in particular, exhibit strong phytotoxic effects (Pikovsky, Y. I., Ismailov, N. M., & Dorokhova, M. F., 2015).

The harmful impact of heavy oil fractions is caused by the formation of a mechanical barrier between seeds, root systems, and the surrounding environment, hindering water-air and nutrient regimes. Soil biota also experiences significant suppression. The effect of oil on soil organisms is largely determined by its concentration. In low concentrations, oil has a stimulating effect on soil biota as it serves as an energy substrate for a large group of microorganisms and contains substances that stimulate plant growth and development. Severe soil oil pollution is accompanied by acute toxic effects on living organisms, especially in the initial period after contamination (Orudzhev, E. F., Avdotin, V. P., & Bryanskaya, I. P., 2018).

The soil cover, a fundamental element of the landscape, is the first to bear the "ecological impact". Developing a methodology to combat soil pollution with oil and oil products is an extremely complex matter (Theoharides, K. A., & Suberg, M., 2019). Soil reactions to oil pollution and their sensitivity to these pollutants differ in various soil zones and within associated landscapes. The main factors include the chemical composition of the contaminant, soil properties and composition, and the physico-geographical conditions of the area.

Soil is a challenging object of analysis, and its organic part is complex and diverse in composition. Any soil contains 1 to 15% organic matter depending on the soil type. Humus constitutes 85–90% of the total organic matter in the soil. Additionally, soils contain nonspecific substances such as fats, carbohydrates (cellulose, pectins, pectosans, mannans, etc.), proteins, amino acids, amides, lignins, tannins, terpenes, resins, etc. (Zhang, J., Fan, S., Yang, J., Du, X., Li, F., & Hou, H., 2014). Therefore, when choosing a solvent, the complex chemical composition of both the determined substance (oil product) and the investigated object (soil) must be taken into account.

The impregnation of soil mass with oil leads to changes in the chemical composition, properties, and structure of the soil. This primarily affects the humus horizon, where the carbon content sharply increases, but the soil's properties as a nutrient substrate for plants deteriorate. Oil products cause the formation of a stable hydrophobic film, thereby disrupting the recirculation and exchange of nutrients through the soil. In the soil profile, changes in redox conditions are possible, an increase in the mobility of humic components, and certain trace elements (Barrosa, F. C. de F., Vasconcellos, L. C. G., Carvalhoc, T. V., & Nascimento, R. F., 2014). Volatile components of oil (substances with a boiling point up to 200 °C) hold a significant place among petroleum-derived substances polluting natural objects. These compounds constitute a substantial portion (20–30%) of the oil composition and are the primary components of many widely used petroleum products (gasoline, diesel fuel, etc.). These compounds are highly toxic and relatively resistant to biodegradation, making them more migratory within landscapes compared to other oil hydrocarbons.

However, the mechanisms of redistribution of a broad spectrum of individual volatile organic substances from oil remain poorly researched in ecosystems. It is believed that the self-cleaning rate of soils from volatile hydrocarbons (VHC) through physical evaporation is sufficiently high, and their study is generally not given due attention (Zhang J., Fan S., Yang J., Du X., Li F., Hou H., 2014). Most commonly used methods for assessing oil pollution do not involve determining the composition and content of volatile components, as they include analytical operations such as soil drying and solvent evaporation after oil product extraction. Currently, there is insufficient data on the composition and content of light oil components in soils and adjacent environments.

The content of VHC in oil-contaminated soils is influenced by various processes, such as physical evaporation, radial and vertical migration, biodegradation, and may be associated with differences in the redistribution and transformation of volatile hydrocarbons on different elements of the meso relief (Francisco Cláudio de Freitas Barrosa, Luiz Constantino Grombone Vasconcellosb, Técia Vieira Carvalhoc, Ronaldo Ferreira do Nascimentoa Removal 2014). The high mobility of volatile oil products can increase the risk of secondary contamination of water bodies through transport with surface and soil waters from adjacent areas. When entering rivers and lakes, oil products can concentrate at the interface between the water and bottom sediments and in the bottom sediments. Consequently, a high content of soluble and hard-to-oxidise oil hydrocarbons in the water may be sustained for a long time due to the influx from bottom deposits.

Research method

In the scope of investigating the long-term negative impact of oil pollution on soil ecosystems, we conducted laboratory studies on the specific composition and concentration of petroleum products. These studies were based on chemical methods: extraction using organic solvents, ignition to determine volatile components, and gas-liquid chromatography.We took samples from two oil-contaminated soils of different degrees from the "Balahanyneft" field. The samples were collected from the well area at two different locations on April 4, 2023.

We studied the processes of extracting petroleum products from the samples using various solvents: benzene, n-hexane, and toluene. For this, we took samples 1 and 2, placed them in a flask, added one of the solvents, stirred in a flask with a reflux condenser for 3 hours at a temperature of 21–22 °C. The extraction for each sample was repeated three times. Then, the extracts were combined and the solvent was evaporated.

Table 1. *Amount of Extracted Petroleum Products by Extraction Method from Oil-Contaminated Samples,%*

Solvents	Samples	
	1	2
Benzene	0.48%	0.12%
Hexane	0.47%	0.11%
Toluene	0.65%	0.18%

The obtained samples of petroleum products after extraction were analysed using gas-liquid chromatography. Among the currently available monitoring methods, the most promising one with simultaneous decryption of the chemical composition is gas chromatography with flame ionisation, allowing the determination of individual components in a mixture of petroleum products, making this analysis method indispensable. Therefore, the samples of extracted petroleum products were analysed using the mentioned method.

Analysis of results

Despite the potentially high self-cleaning rate of contaminated soils from volatile hydrocarbons through physical evaporation in the climatic conditions of our region, and considering the limited data on the composition and content of light components in soils and similar environments at the moment, we decided to determine the composition and content of volatile components. The content of these components is significant, reaching up to 0.56%, and these compounds are characterized by high toxicity, relative resistance to biodegradation, and migratory capability in the soil compared to other hydrocarbons. The mechanisms of their distribution in ecosystems remain poorly studied.

For a qualitative and quantitative characterization of the degree of contamination of samples with light-volatile hydrocarbons, we conducted the following studies. We took 5 portions of each sample, placed them in porcelain crucibles, and subjected them to ignition at 100, 200, 300, 400, and 500 °C. Initially, we obtained data on the moisture content of these soil samples, followed by the evaporation of hydrocarbons with different boiling temperatures. Essentially, we studied the content of light-volatile components. The data are presented in Tables 2 and 3.

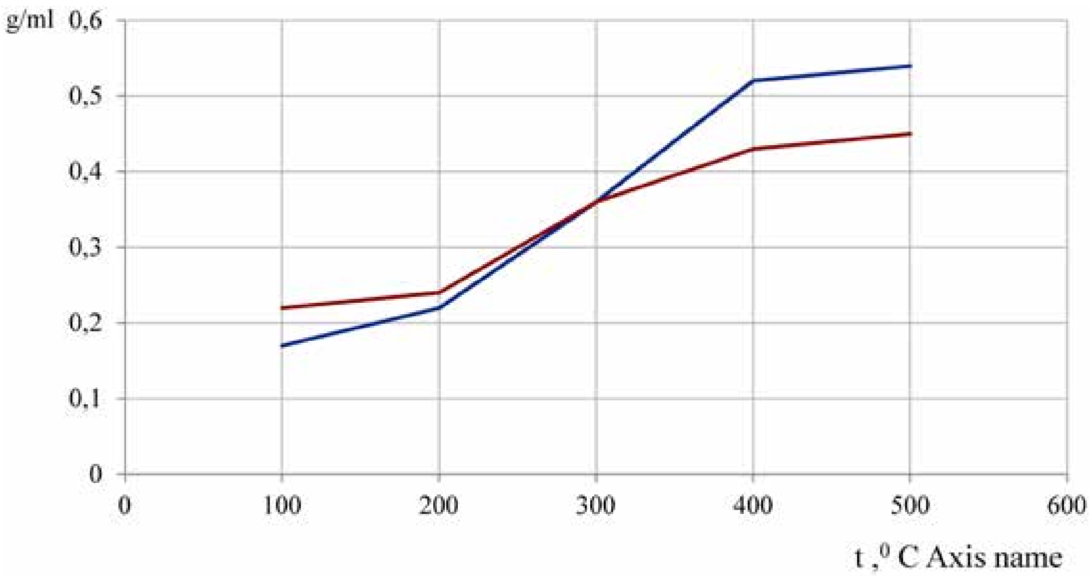
Table 2. *Content of Volatile Components in the Sample, g/ml*

Samples	Temperature, ^{0} C				
	100	200	300	400	500
A_1	0.17	0.19	0.38	0.52	0.55
B_1	0.19	0.24	0.40	0.51	0.53
C_1	0.16	0.23	0.38	0.53	0.55
D_1	0.17	0.23	0.22	0.4	0.51
E_1	0.18	0.20	0.42	0.55	0.56

Table 3. *Content of Volatile Components in the Sample, g/ml*

Samples	Temperature, ^{0} C				
	100	200	300	400	500
A_2	0.22	0.24	0.34	0.49	0.53
B_2	0.24	0.25	0.39	0.48	0.50
C_2	0.20	0.22	0.35	0.43	0.44
D_2	0.21	0.24	0.38	0.41	0.43
E_2	0.22	0.23	0.32	0.34	0.36

Figure 1. *Content of Volatile Components*



Conclusion

The research findings revealed that the content and composition of volatile components significantly vary depending on the sampling location of soils and the duration of contamination. Alongside heavy hydrocarbon fractions, the taken samples contain a certain amount of moisture and volatile toxic hydrocarbons (ranging from 0.17 to 0.56%).

Despite the existence of various methods for cleaning oil-contaminated soils, extraction remains the most effective physico-chemical method to date. In the future, we plan to enhance its efficiency through additives. In this study, organic solvents were applied as extractants, extracting petroleum products up to 0.65%. The extracted petroleum products can undergo additional industrial processing.

Even if land plots containing a large amount of petroleum products do not occupy extensive areas in a territorial context, they serve as constant sources of environmental pollution. Oil-contaminated soil mixtures with a high coefficient have the ability to form stable complexes, which, due to the gradual decay of heavy hydrocarbons over an extended period, become sources of hydrocarbon emissions. Considering that these sources of environmental pollution are located in densely populated areas of the Absheron Peninsula, eliminating these sources makes their urgency even more acute.

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submitted 22.08.2023;
accepted for publication 20.09.2023;
published 8.10.2023

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