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FREE AND BOUND LIPIDS IN TYPICAL CHERNOZEMIC SOIL IN THE TERRITORY APPROPRIATE TO ACTIVE OIL CLUSTER WELLS

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ABSTRACT

All technological processes used in petroleum industry (i.e. exploration, drilling, production, refining and transportation) cause soil contamination. Oil pollution can cause adverse and irreversible changes in soil ecosystems. The major soil self-cleaning process is biodegradation; however, paraffins, asphaltenes and tars are quite resistant to environmental microbial degradation. Their transformations are long-term and the least explored, that is why evaluation of these components' concentrations in humus soils exposed to continuous systematic pollution is of particular interest. This paper addresses evaluation of lipid free and bound fractions in top layers of chernozemic soils surrounding oil producing well clusters.

Keywords: lipid free and bound fractions, chernozemic soil, oil pollution, fossil water, well cluster, Soxhlet extractor, organic carbon.

1. INTRODUCTION

All technological processes used in petroleum industry (i.e. exploration, drilling, production, refining and transportation) cause soil contamination [1, 2]. Petroleum hydrocarbons are one of the most ecologically dangerous pollutants. Oil pollution can cause adverse and irreversible changes in soil ecosystems. A regular supply of petrochemicals leads to soil adaptation and restructuring of both microbial community and soil organic matter [3, 4, 5, 6, 7].

The major soil self-cleaning process is biodegradation; however, paraffins, asphaltenes and tars are quite resistant to environmental microbial degradation. Their transformations are long-term and the least explored, that's why evaluation of these components' concentrations in humus soils exposed to continuous systematic pollution is of particular interest.

Land ecosystems (soils primarily) are the most vulnerable to oil pollution.

Petroleum hydrocarbons can end up in the soil for a variety of reasons, for example oil seepages during production, refining or transportation. Sorption capacity and capillary flow make soil the main depositional environment for the hydrocarbons. Once in the soil, the hydrocarbons can further spread to the adjacent environments: atmosphere (evaporation), flora (absorption by the root system) and ground water (filtration).

Oil pollution causes grievous ecological damage: reduced soil fertility, groundwater contamination, extensive plant mortality, etc. [8]. This problem is particularly acute in Russia because of well-developed petroleum industry and huge petroleum pipeline system. At the present time, about 800 thousand hectares of Russian soils need to be rehabilitated [9].

Lipids are organic matters which are insoluble in water but soluble in nonpolar organic solvents (hexane, benzol, chloroform) [10]. They are a mixture of fatty acids, sterols, terpenes, long-chain hydrocarbons, chlorophyll, fats, wax and resins [11]. Thus, lipids are substances grouped by the solubility and not their basic structure [12]. Lipids affect physical properties of soils, but there is almost no data on the subject [13].Lipids are hydrophobic and should reduce water absorption capacity of soils.

We know a lot more about chemical properties of lipids, though [13]. The majority of high-molecular organic acids of the lipid group contain hydroxyl and carboxyl groups (for example, palmic and stearic acid).Small quantities of organic acids may also be present in soil rhizosphere. Depending on pH, the functional groups of organic acids (OH and COOH) can dissociate, and therefore these substances can contribute to cation exchange reactions and complexing reactions.

The objective is to estimate the free and bound lipid contents in top layers of typical chernozemic soils surrounding well clusters.

2. MATERIALS AND METHODS

This study focuses on typical chernozemic soils that can be found within the Ulyanovskoye oilfield (Devonian sediments) which is located in the south-east of the Republic of Tatarstan and has been developed since 1972.The soil samples used in this project were taken in Cheremshan district (2 km south-east of village Kutema) in the autumn of 2011.In this district, and in the region as a whole, there is no petroleum production culture as such. The research covered a typical production site equipped with well clusters and horse-head pumps. It is located so that the surface water flow first passes through a long shallow depression and then enters a stream valley covered with vegetation. The samples were taken from the top layers of contaminated soils around the well clusters and within the arable lands exposed to systematical pollution with fossil water. Samples of arable and fallow soils were also included in the study. A map of the study area is shown in Figure-1.

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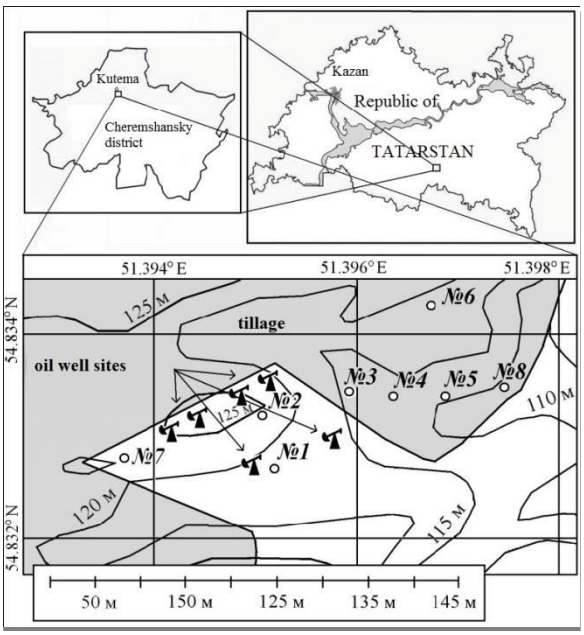

Figure-1. Map of the study area and sampling points.

Intact (baseline) soils are typical chernozemic soils (medium thick, clay-loamy, laying on yellow-brown calcareous loam).

Figure-2 shows a photo of a cultivated chernozemic soil. In accordance with good petroleum production practice, horse-head pumps undergo maintenance and repairs once every three years. Pipes are extracted, and fossil water is spilled. The photo shows that pea seeds do not grow within the area of the fossil water drainage (this can be considered a biotest).

The samples were taken inbatches in accordance with the level of human-induced impact. Samples №1 and №2 were taken within the borders of the industrial site; samples №3, №4 and №5 were taken from the arable soil subjected to systematic fossil water pollution; samples №6 and №7 were taken from the intact fallow soil. The samples were cut into small (10x20 cm) rectangular bricks and packed in plastic containers. Then, they were separated into samples taken from 0-10 cm depth and 10-20 cm depth.

Dried samples were then quartered, and average samples were prepared for further analysis. The average samples were then crushed to powder (particle size <0.25 mm).

Lipid fractions were defined as substances soluble in chloroform, as given in [14]. Soil samples in tracing paper envelopes (~35 g each) were dried in an oven (50 °C, 48 h), then packed in filter paper thimbles, previously flushed with chloroform in Soxhlet extractor (for 24 h). The exact weight of each sample was calculated as a difference between the weight of envelopes filled with samples and empty envelopes.48-hour Soxhlet extraction was conducted to isolate the free lipid fraction.

The extracts were then concentrated via steam stripping, supplemented with chloroform to the necessary volume and sealed with plastic plugs in 100 ml capacity measuring flasks. General free lipid extraction scheme is presented in Figure-3. Next, the thimbles were removed from the extractor and the soil was first dried in the open air for 3 days and then - in the oven (50 °C, 48 h). The soil samples were then moved to plastic containers and treated with an aqueous solution of 2.5% HF and 2.5% HCl (for 48 h); the residue was flushed with water to pH 5.0, dried in the open air and in the oven (50 °C, 48 h).Then the second Soxhlet extraction was conducted in order to isolate the bound lipid fraction.

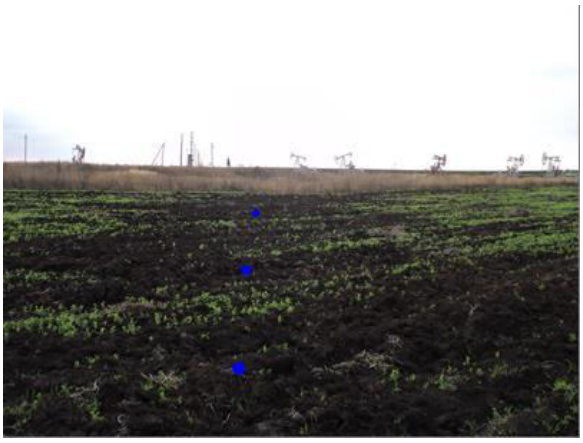

Figure-2. Arable chernozemic soil (№3, №4, №5 - from top downward).

The carbon content in soils and lipid fractions was determined via wet combustion of $K_2Cr_2O_7$ in a mixture of concentrated H_2SO_4 and 85% H_3PO_4 (3:2) in test tubes of special construction [15]. The content of CO_2 absorbed in the alkali solution was determined via titrimetry. When analyzing the lipid fractions, extract aliquots were placed in the test tubes, concentrated and dried in the oven (50 ° C, 48 h). The carbonate-related carbon content was determined using the same samples in test tubes.

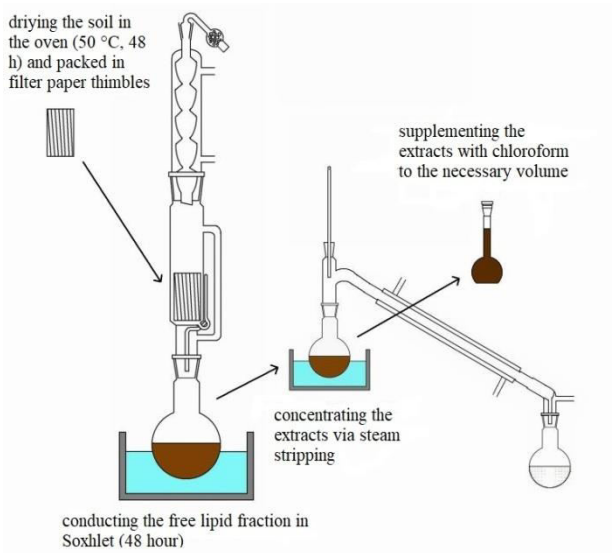

Figure-3. General free lipid extraction scheme.

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3. RESULTS AND DISCUSSIONS

The most useful approach is to determine the organic carbon content in the original soil samples and the dried extract aliquots using any direct method based on combustion and quantification of the released CO_2.We chose the method proposed by Snyder and Trofimov [15]. The analysis is carried out as follows. A soil sample is placed on the bottom of a large thick-walled test tube and covered with 1 g of potassium bichromate. Then, 25 ml of a mixture of concentrated H_2SO_4 and 85% H_3PO_4 (3:2) is added. Next, a trapwith 2 ml of 2 mol/l NaOH is quickly placed in the test tube. The trap is stuck in the upper part of the test tube. Then, the test tube is sealed with a syringe plunger. The plunger is fixed with a soft copper wire (originally, glass test tubes with screw tops were used).The test tube is then heated at 120 °C for 2 hours. For this purpose, a water thermostat filled with glycerin was used. After 12 hours, the CO_2 trap is removed from the test tube and 2 ml of 1 mol/l $BaCl_2$ and 5 drops of phenolphthalein are added to the trap. Next, the tube contents are titrated using a microburet with 1 mol/l HCl. The following formula is used for calculations:

absorbed C(mg) = (HCl(ml) in the blank analysis × K − HCl(ml) in the sample analysis × K) × 6.

Turns out the oxidizing method where organic carbon content is estimated at the reducing amount of oxidant usually produces erroneously low results. On average, the difference is about 6% (11% max).

This pattern is reflected in the organic carbon content scatter diagram (Figure-4). The majority of points are shifted toward the vertical axis displaying the values obtained using the Snyder and Trofimov method.

Hydrochloric acid used in pre-treatment frees the cation-bound lipids, and hydrofluoric acid is used to free the lipids bound to the organo-mineral matrix [14]. However, the content of this fraction does not exceed 2% of the total carbon content in polluted soils, and 0.5% in baseline soils. Therefore, the total lipid content was used in further analysis.

The bar graph presented in Figure-5 clearly shows that the total lipid content in arable soils subjected to systematic pollution (samples №3, №4 and №5) is substantially higher than that in baseline arable soils (№6) and baseline fallow soils (№7).The total lipid content is 7 times higher at the point closest to the industrial objects (№3), and 5 times higher at the furthest point (№5).

Difference between arable soils subjected to systematic pollution and baseline arable soils can be expressed in the lipid (free lipids + bound lipids) carbon share in total organic carbon content. It can reach 26% in points closest to the industrial objects (№3).

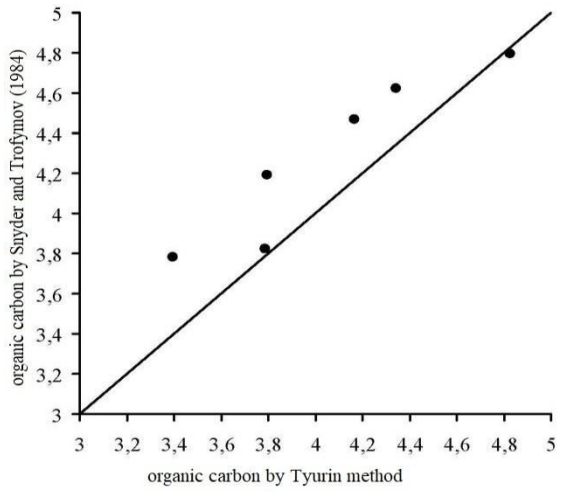

Figure-4. Organic carbon content scatter diagram obtained using the Tyurin method and the Snyder and Trofimov method.

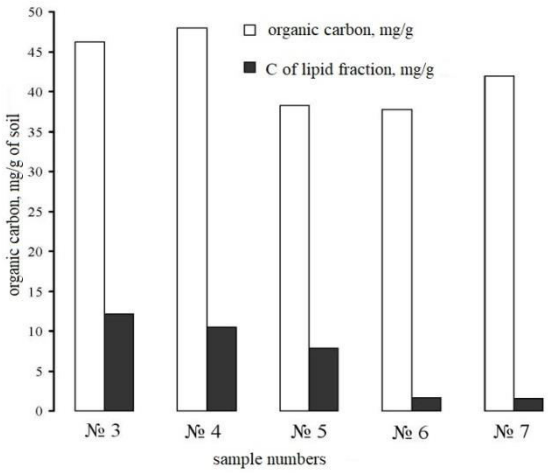

Figure-5. The total organic carbon content and the lipid carbon content in the 0-10 cm layer of chernozemic soils ranked by the level of anthropogenic load.

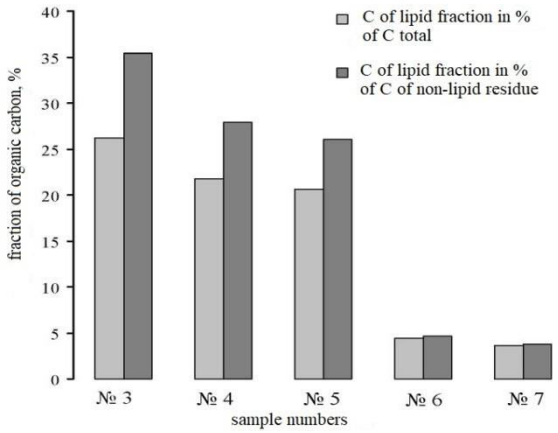

Figure-6. The lipid carbon share in the total organic carbon content in the 0-10 cm layer of chernozemic soils, ranked by the level of anthropogenic load.

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CONCLUSIONS

A Soxhlet extraction was carried out to separate free and bound lipid fractions in the samples taken from the top layer of typical chernozemic soils around the well clusters at points ranked by the level of anthropogenic load.

It was found that the total lipid (free lipids+bound lipids) carbon content in the upper layers of arable soils subjected to system atic pollution is 5-7 times higher than that in baseline arable soils and fallow soils.

It was also found that the share of lipid carbon content in total organic carbon content can range between 1/4 and 1/3.

ACKNOWLEDGMENTS

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