Age-old transformation of oil hydrocarbons in polluted Grey-Brown Soil in the Absheron Peninsula

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Abstract. Oil production, transportation and refining are a source of the extensive environmental pollution. The study of oil pollutants allows the identification of their behavior pattern necessary in order to elaborate efficient decontamination technologies. The Absheron oil field is one of the most long-term exploited deposit in the world. Today this area is a unique place to investigate the long-lasting natural oil transformation processes. Grey-Brown Soils contaminated with crude oil 100 and 40 years ago and currently were investigated. Hexane-extractable fraction of oil compounds was examined by chemical methods, gas chromatography and mass spectrometry. In the process of natural degradation, molecular weight of oil hydrocarbons and degree of oxidation significantly increased, while the contents of carbon and hydrogen slightly decreased with time. The results obtained have shown the accumulation of high-molecular weight aromatic molecules with high degree of unsaturation in the upper layer of the soil contaminated 100 years ago. These aromatic structures exhibit the great resistance to decomposition and may be carcinogenic, thus posing a risk to human health. The contamination with oil resulted in altering soil properties. More pronounced change was observed in the soil carbon, including the soil contaminated 100 years ago. Over time after contamination, the soil alkalinity enhanced, whereas soil pH did not change. Our study evidences that oil pollutants continue to be present and the soil properties have not recovered even 100 years after pollution. Reclamation of these areas requires the application of special technologies.

1. Introduction

Soil contamination with oil spills is a global challenge today. Crude oils contain literally hundreds of different chemical compounds depending on the unique geological history involved in the formation of an oil deposit. Generally oils consist of n-alkanes, isoprenoid hydrocarbons, aromatic hydrocarbons, resins and asphaltenes [1]. The presence and proportion of different classes of oil hydrocarbons (HCs) is specific feature of any oil.

Azerbaijan is one of the oldest oil producers in the world [2]. The Absheron Peninsula is located in the eastern Azerbaijan, along the western coast of the Caspian Sea. The first oil well was drilled in Absheron in 1847 by a primitive percussion drilling tool [3]. By the end of the 19th century Absheron was the main oil producer, providing 97.7 % of Russian oil in 1890 and half of global production in 1901. Large areas in Absheron were contaminated by crude oil for more than 150-year period, so today aged oil contaminated soils can be used for investigation of the natural oil transformation.

Since entering soil, oil compounds undergo the processes of natural weathering, including evaporation, migration, dissolution, and biodegradation. The degradation rate and fate of oil pollutants depend on numerous factors, among which are oil composition, pollution load, soil-climatic conditions and others. Microbial degradation provides major contribution to natural oil attenuation. Oil compounds
highly differ in their susceptibility to biodegradation. The biodegradability of oil HCs is ranged as follows: linear alkanes > branched alkanes > small aromatics > cyclic alkanes [4]. High-molecular weight polycyclic aromatic hydrocarbons, tars and resins are extremely resistant to degradation.

The oils from Absheron deposit are characterized by specific homologous series of n-alkylcyclohexanes and n-alkylcyclopentanes. Tricyclic saturated hydrocarbons belonging to the class of naphthenes are prevalent in the oil composition [5]. Adamantane and its closest homologues (1-, 1,3- and 1,3,5-methylsubstituted adamantanes) as well as the tetracyclic structures belonging to the sterane hydrocarbons with a ratio of $C_{27}:C_{28}:C_{29} = 28:33:38$ are typical to the Absheron's oils [6].

Soil characteristics, such as texture, pH, nutrient supply, water-holding capacity, oxygen availability, and climatic conditions are essential factors that control the transformation and decomposition of oil HCs.

The Absheron Peninsula is characterized by a temperate semi-arid climate with average year temperatures from +10 to +14.5°C with minimum in January (-1-+5°C) and maximum in July (+21-+27 °C). The precipitation level is around or less than 200 mm. The summarizing solar radiation is about 130-135 kcal cm$^{-2}$ year$^{-1}$. Grey-Brown Soils dominate in the soil cover. These soils develop in the arid steppe zone, at 50-200 m height of sea-level, low hills plateaus on the calcareous and gypsum loams.

To mitigate negative environmental consequences and a threat to human health, elucidation of the rate, direction and peculiarities of transformation processes of oil pollutants is an important task of both fundamental and applied sciences [7]. To study the long-term behavior of oil HCs in the environment is also necessary for developing proper reclamation technologies.

The aim of our study was to investigate the processes of natural oil transformation in the contaminated Absheron's soil and resulting alteration in soil properties over a 100-year period.

2. Materials and Methods

The study was carried out on 3 sites of former oil wells in the Absheron Peninsula, operating 100 years ago, 40 years ago and currently. All selected sites initially had similar type of soil, relief, and parent material. The top layer of native Grey-Brown Soil was characterized by low organic matter (0.95% of Corg), neutral pH (6.7), low cation exchange capacity (5.6 meq/100 g). The soil contained 15% of sand, 35% of clay and 45% of loam. The contents of clay and loam increased with depth and the sand content gradually decreased.

The plant cover was typical for semi-desert ecosystems with a predominance of Seidlitzia florida, Artemisia and Alhagi. Experimental sites were located at a distance of less than 1 km. Besides contaminated soils, unpolluted soil was sampled as well. Soil samples were dried at +65°C for 24 h, ground and passed through a 0.2 mm sieve.

Soil was analyzed for hexane (C$_6$H$_{14}$)-extractable fraction of HCs using ST 255 Soxtec system (FOSS). The elemental composition of C$_6$H$_{14}$-extracted HCs (C, H, N, O, S) was determined by elemental analyzer Vario El III (Elementar, Germany). Average molecular weight of C$_6$H$_{14}$- extractable HCs was measured by the method of cryoscopy [8].

Molecular structures of C$_6$H$_{14}$-extractable fraction of HCs were analysed using the gas chromatography (Chromatek K5000, Russia) with mass spectrometry detector ISQ (Thermo Scientific) [9].

The following chemical soil properties were tested: total carbon (C$_{org}$); pH, soil alkalinity (HCO$_3$) by standard methods and Fe and Mn by the method of Mehra and Jackson [10]. The concentration of carbon dioxide (CO$_2$) in soil samples was measured directly by gas chromatograph (Chromatek K5000, Russia).

Each analysis was conducted in 4 replications. All data obtained was subjected to a statistical analysis based on comparative methods using Duncan’s multiple range tests for mean separation at the 5% level of significance [11].

3. Results and Discussion

The maximum content of C$_6$H$_{14}$-extractable fraction of HCs was determined in the upper horizon of recently contaminated soil (12.4±0.3%). It gradually decreased down the soil profile and amounted to...
1.5±0.2% at a 2-m depth. In the soil contaminated 40 years ago, the content of C₆H₁₄-extractable HCs was 5.0±0.3% in the surface horizon and 3.3±0.2% at a depth of 20-80 cm. In the 100-year-old contaminated soil, the contents of HCs reached 3.7±0.2% in the surface layer and varied within 0.5-3% in deeper layers, remaining significantly higher than those in uncontaminated soil (less than 0.01%).

Elemental composition and average molecular weight of the C₆H₁₄-extractable fraction of HCs are presented in Table 1. The carbon and hydrogen contents in the tested fraction were similar in the soils contaminated currently and 40 years ago. But in the soil contaminated 100 years ago, the carbon and hydrogen were significantly less, while the oxygen content was remarkably increased, which indicates oxidation of oil compounds. The contents of nitrogen and sulphur in the HCs fraction remained almost unchanged for a 100-year period.

An average molecular weight of organic molecules extracted from contaminated soils significantly increased over the period of degradation.

Table 1. The elemental composition and average molecular weight of C₆H₁₄-extractable fraction of HCs.

| Depth, cm | C   | H   | N   | O   | S   | Mₙ* |
|----------|-----|-----|-----|-----|-----|-----|
|          | %   | %   | %   | %   | %   |     |
|          |     |     |     |     |     |     |
| Modern contamination | | | | | | |
| 0-16     | 85.0| 12.0| 0.30| 2.20| 0.50| 490 |
| 16-60    | 84.3| 12.4| 0.30| 1.50| 0.30| 390 |
| 60-77    | 84.6| 12.6| 0.30| 1.00| 1.60| 420 |
| 40-years-old contamination | | | | | | |
| 0-10     | 85.1| 12.0| 0.20| 2.35| 0.35| 540 |
| 10-60    | 85.6| 12.2| 0.20| 1.55| 0.35| 435 |
| 60-80    | 87.3| 11.2| 0.20| 1.00| 0.30| 370 |
| 100-years-old contamination | | | | | | |
| 0-7      | 81.7| 11.5| 0.30| 6.20| 0.30| 570 |
| 42-55    | 82.5| 11.7| 0.20| 5.20| 0.40| 515 |
| 55-69    | 82.0| 11.6| 0.20| 3.90| 0.30| 560 |
| Crude oil| 86.8| 12.1| 0.20| 0.60| 0.30| -   |
| LSD₀.₀₅  | 1.0 | 0.2 | 0.10| 0.05| 0.05| 20  |

Mₙ* - average molecular weight

The results of mass spectrometry showed that long-term transformation of oil compounds in the soil resulted in the accumulation of high molecular weight compounds with condensed aromatic structures, containing 5-6 rings, and high degree of unsaturation. The maximum content of aromatic HCs was determined in the surface layer of the soil contaminated 100 years ago. Their content was reduced with depth. The accumulation of such molecules poses a threat to human health because they are known to be carcinogenic [12].

Selected soil chemical properties are presented in Table 2. The comparison analysis of oil-polluted and unpolluted soils has demonstrated that in general soil alkalinity, acidity and cation exchange capacity did not alter. In modern contaminated soil the mobile forms of Fe and Mn were significantly reduced as compared to unpolluted and old contaminated soils. The same regularity was found for the CO₂ concentration. The production of CO₂ reflects the activity of soil microorganisms. The oil contamination inhibited microbial activity resulting in reduction in the CO₂ concentration and in mobile forms of Fe and Mn in the soil. Our results evidence that the soil microbial activity was restored in 40 or 100 years after pollution.

The oil pollution caused remarkable increases in the total C in the soil. Higher values of Corganic were observed in upper layers and it was gradually reduced with soil depth. The Corganic declines very slowly
with time and the soil contaminated 100 years ago continues to contain much organic matter in comparison with unpolluted one.

### Table 2. Selected chemical properties of unpolluted and oil-polluted Grey-Brown Soils.

| Depth, cm | C$_{org}$, % | pH | Alkalinity, HCO$_3^-$ | Fe, % | Mn, % | CO$_2$, % |
|-----------|---------------|----|------------------------|-------|-------|-----------|
|           |               | H$_2$O | KCl | mg eq$^{-1}$ |       |       |           |
| Unpolluted soil |                |         |     |            |       |       |           |
| 0-25      | 0.95          | 6.7    | 7.5 | 0.232      | 0.014 | 0.35 | 0.018   | 5.39   |
| 25-50     | 0.52          | 6.8    | 7.4 | 0.448      | 0.027 | 0.40 | 0.024   | 9.49   |
| 50-75     | 0.58          | 6.8    | 7.5 | 0.133      | 0.008 | 0.42 | 0.019   | 4.46   |
| Modern contamination |                |         |     |            |       |       |           |
| 0-16      | 14.11         | 5.8    | 7.8 | 0.250      | 0.015 | 0.13 | 0.006   | 0.37   |
| 16-60     | 11.98         | 6.4    | 7.6 | 0.525      | 0.032 | 0.15 | 0.009   | 2.05   |
| 60-77     | 6.13          | 6.1    | 7.9 | 0.150      | 0.009 | 0.18 | 0.007   | 1.30   |
| 40-years-old contamination |                |         |     |            |       |       |           |
| 0-10      | 7.82          | 6.7    | 7.5 | 1.025      | 0.063 | 0.57 | 0.031   | 5.39   |
| 10-60     | 4.38          | 6.8    | 7.4 | 0.950      | 0.058 | 0.43 | 0.023   | 9.49   |
| 60-80     | 4.21          | 6.7    | 7.6 | 0.800      | 0.048 | 0.47 | 0.011   | 7.63   |
| 100-years-old contamination |                |         |     |            |       |       |           |
| 0-7       | 10.06         | 6.5    | 7.2 | 0.825      | 0.050 | 0.31 | 0.014   | 5.95   |
| 7-42      | 1.64          | 6.6    | 7.5 | 0.725      | 0.044 | 0.73 | 0.029   | 5.98   |
| 42-55     | 5.61          | 6.2    | 7.1 | 0.675      | 0.041 | 0.21 | 0.009   | 2.23   |
| 55-69     | 3.29          | 6.6    | 7.5 | 0.750      | 0.046 | 0.47 | 0.024   | 4.28   |
| LSD$_{0.05}$ | 0.15 | 0.1    | 0.1 | 0.025      | 0.005 | 0.04 | 0.003   | 0.04   |

Due to highly different degradability of oil components, the molecular structure of oil pollutants controls primarily their transformation. The Absheron's oils have several specific characteristics: high densities, ranging between 0.917 and 0.925 g cm$^{-3}$; the acid value of 2.88-3.75 KOH g$^{-1}$; kinematic viscosity at 100°C 9.76-10.23 mm$^2$ s$^{-1}$, flash point +118-+120°C, freezing point -7—10°C and distillation onset point - +238-+248°C [5]. The absence of low molecular weight n-alkanes and the prevalence of saturated polycyclic alkanes in Absheron's oils coupled with local soil-climatic conditions inhibit the processes of self-purification, leading to elevated levels of pollutants even 100 years after contamination. To restore the local ecosystems, feasible decontamination technologies should be used.

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