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The Impact of Oil Contamination on Soil Ecosystem

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Abstract: The laboratory analyses have revealed increased concentrations of total petroleum hydrocarbons, polyaromatc hydrocarbons, asphaltenes and heavy metals in soil samples collected from different parts in the territory of the Absheron oil fields. Soil pollution reaches 1,5m depth in the majority of samples. The results of microbiological studies carried out to evaluate the effect of toxic discharges on soil biological properties showed that long-term anthropogenic impact has significantly reduced the self-purification capacity of oil contaminated soils in the Absheron industrial region.

Keywords: Absheron peninsula, hydrocarbons, soil contamination, microorganisms, heavy metals

1. Introduction

Oil and oil products are the most priority pollutants of the environment because of their toxicity, spreading scale and high migration ability. Oil fields' development and exploitation, and violation of the hydrocarbon transportation rules result in the pollution of natural ecosystem, particularly soil cover.

Along with other hydrocarbon bearing regions of the world, the problems of environmental pollution are characteristic also for the Absheron peninsula of Azerbaijan Republic, where a major part of the country's industrial potential, including 60% of onshore oil production, is located. The territory is also a place of important oil and gas transportation pipelines (Khalilova, 2013).

The history of more than 150 years' oil production has severely reflected on the landscapes of the peninsula. Long-term contamination of soils by crude oil, produced water and drill cuttings and the consequent environmental impact has changed geochemical, hydrological, geophysical and biological conditions of ecosystem throughout the region that have been reported by a number of authors (Alekperov, 2000; Mamedov and Aliyev, 2005; Isaev et al., 2007; Aliyev and Khalilova, 2014). In this respect, the studies relating to the impact of technogenic waste of various etiologies on the biological processes of individual soil types are of significant importance (Samedov et al., 2011).

Taking into consideration the fact that the production and transportation of hydrocarbon reserves are continuously increasing, anthropogenic impact on the environment is expected to increase in the future years.

In order to find a perfect solution to the problem, it is expedient to carry out studies on individual pollutants and evaluate their negative impact on soil ecosystem.

A primary goal of this work, therefore, was to study the degree of contamination of gray-brown soils with oil hydrocarbons and heavy metals and the effect of oil contamination on the soil microbiological properties in the territory of Absheron oil fields.

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2. Material and Methods

The studies were carried out on the territory of Absheron oil and gas fields. The data presented in this paper covers the researches implemented on Zykh-Hovsan and Bibieybat fields of the Contract area. Soil samples were collected from distinct sites selected after visual observations depending on the pollution degree. Observations were performed on both visible surface polluted areas and top geodesic maps of the former drilling wells. Basic attention was paid to the vicinity of oil fields, oily lakes and drill cutting storage sites. Holes were dug mechanically using portable instrument. The depth of sampling for chemical analysis was 0,25 m. The samples were analyzed for heavy metals, total petroleum hydrocarbons, polyaromatic hydrocarbons and asphaltenes according to generally accepted test methods (USEPA Test methods for Evaluating Solid Wastes, 1986):

- concentration of total petroleum hydrocarbons (TPH) - aliphatic, alicyclic and aromatic hydrocarbons - was determined by gas chromatography method (GC);
- concentrations of USEPA 16 PAHs and 2-6 rings polyaromatic hydrocarbons were determined by gas chromatography –mass spectroscopy (GC-MS) method;
- asphaltenes were analysed by gravimetric method;
- Inductive Coupled Plasma –Optical Emission Spectrometry (ICP-OES) method was used in the analysis heavy metals (As, Ba, Cd, Cr, Cu, Fe, Mn, Pb and Zn), except Hg that was analyzed by Cold Vapour Atomic Fluorescence (CVAF) method.

Standard methods (Ismailov, 2006; Nikitina, 1991) were used to study soils' microbiological properties including respiration intensity, coefficient of hydrocarbon mineralization, the numbers of heterotrophic microorganisms and hydrocarbon oxidizing microorganisms.

3. Results and Discussion

Table 1 presents the generalized data derived from analyses for evaluating the content of hydrocarbons in soils. The data shows increased levels of total petroleum hydrocarbons, 2-6 rings polyaromatic hydrocarbons, and asphaltenes throughout the study site. The highest level of hydrocarbon pollution is detected in the samples taken along oily lake, where the pollution degree varied from 15 until 27% (sample 4). There were several suppressed wells within the study area. Wells have been operated in this area for long time. Despite the wells were suppressed many years ago, the territory was subject to technogenic impact of oil spills, drill cuttings and other pollutants. Their accumulation in soil has resulted in the pollution of these sites by a wide complex of toxic organic substances (samples 7,8).

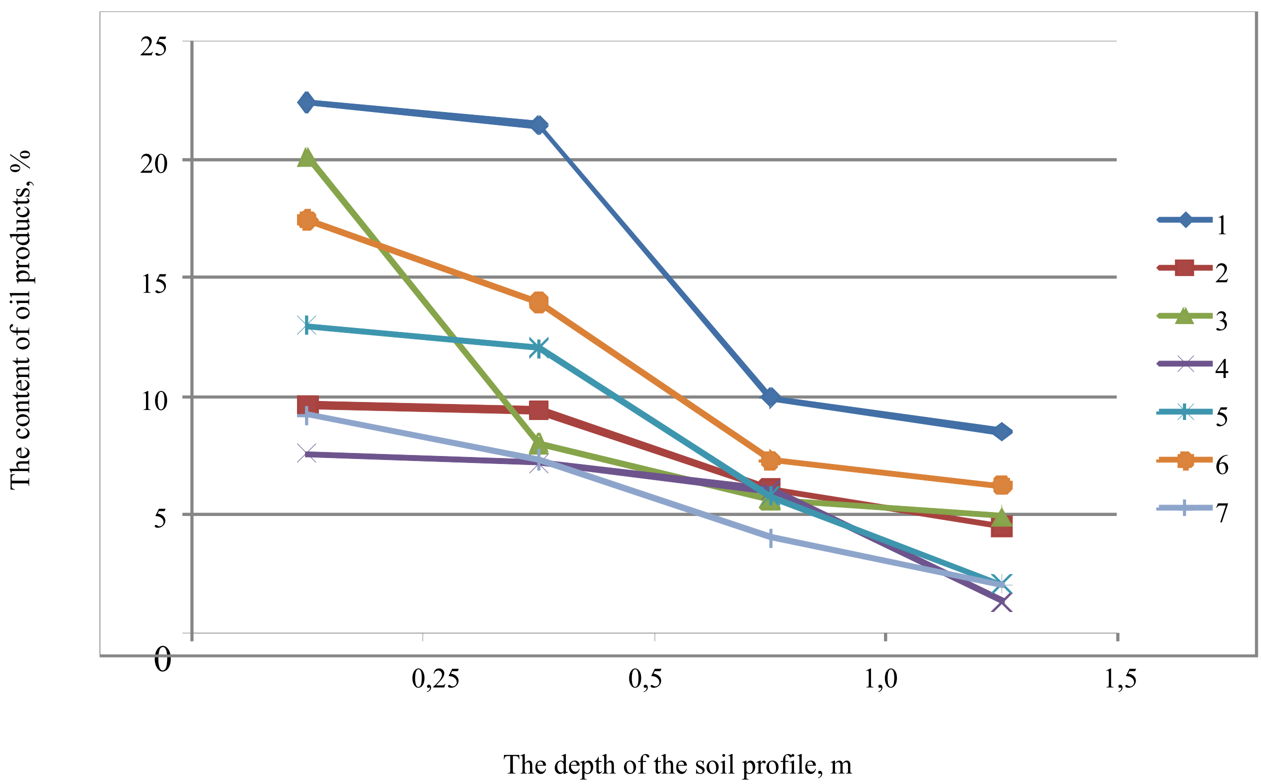
More detailed analyses confirmed the presence of individual toxic PAHs, such as pyrene, benzo(a)pyrene, phenanthrene and chrysene, etc. in majority of samples. The content of these substances varied within wide limits, from 0,0 to 33820 ng/g (Khalilova, 2006). It is known that microbial degradation of PAHs is difficult and long-term process. Several PAHs are mutagenic and carcinogenic and exposure to this group of compounds has been identified as risk factor on both wildlife and human (Mayer et al., 2011; Hites et al., 1977; Duxbury et al., 1997). Considerable levels of total hydrocarbons and asphaltenes were detected also at conditionally non-polluted site (sample 5).

Table 1. Content of hydrocarbons in oil contaminated soils

Samples	Concentration, mkg⁄g dry weight				
	THC	US EPA 16 PAH	NPHD*	2-6 rings PAH	Asphaltenes
1	119858	16,3	54,2	191,8	75,3
2	101728	15,8	118,5	280,8	71,0
3	83607	10,6	220,1	254,0	55,2
4	132079	853,2	10038	12626	119,9
5	1071	0,1	0,2	0,73	4,72
6	85975	16,4	335,8	379,1	69,9
7	47265	2,8	14,9	28,0	4,5
8	18416	0,7	2,1	11,9	3,41

*Note: NPHD- total naphthalene, phenanthrene, and dibenzo-thiophene

Oil and oil products are characterized by high migration ability and penetrate into deep horizons of soil.There have been cases of large-scale hydrocarbon accumulation in soils in the territories of oil-gas production enterprises, refineries, transport pipelines and accidental spills.



Pic. 1. Change in the percentage of oil in the soil depending on the depth of soil profile

In assessing the environmental situation relating to oil contamination, it is important not only to determine the spread of pollution, but also the depth of its penetration (Rogozina, 2006; Pikovskiy, 1988).

A series of analysis was conducted to study soil contamination at depth from 0,25 to1,5 m. It has been established that the contamination of soil in deep horizons varies in a wide range and reaches 1,5m depth. The results of studies have shown that the degree of soil contamination also changes widely within the same study site.

During the research conducted in the territory of one oil and gas production enterprise at Bibieybat field the total content of hydrocarbons in soil samples varied from a minimum 1,3% to a maximum 22,4% depending on the depth of soil profile (Fig. 1). Compared with the lower layers, high concentrations of oil were found in the upper layers of soil profiles (0,25 m), where the average oil content was 13%. The obtained results are significantly higher than the background values (100 mg/kg, i.e. 0,01%) of petroleum compounds for oil polluted soils in the republic.

Most oils have certain content of metals. Tars and asphaltenes constitute of group of trace elements including metals. Concentrated in asphaltenes and tars heavy metals can cause negative impact on the environment. Some of them like Pb, Cd, Hg, Zn and Cu can be very toxic to the ecosystem. Majority of heavy metals have strong affinity for sulfur and disrupt enzyme function forming bonds with sulfur groups in enzyme. They are highly persistent and can easily enter a food chain until reach toxic levels. These may eventually kill many species of fish, birds and mammals (Qiu, 2011).

10 soil samples were therefore analyzed for heavy metals including potentially toxic elements - As, Cd, Cr, Hg, Pb, Cu, Zn, Mn, Fe and Ba. The values derived from the analyses were compared with both the background concentrations (BC) and maximum permissible concentrations (MPC) of these elements established by the Cabinet of Ministers of the Republic of Azerbaijan. The results are presented in Table 2.

Table2. Concentration of heavy metals in oil contaminated soils

Samples	Heavy metals (mg/kg)									
	As	Ba	Cd	Cr	Cu	Fe	Mn	Hg	Pb	Zn
1	5,8	730	0,28	20,4	67,1	16500	380	0,04	27,2	60,7
2	7,6	214	0,10	27,1	30,7	30600	494	0,03	25,3	32,5
3	5,4	1290	0,41	21,6	44,4	28600	691	0,11	37,3	105
4	8,2	335	0,09	27,7	26,6	15500	541	0,07	27,2	54,9
5	7,6	330	0,12	14,4	20,8	16200	294	0,02	26,2	17,1
6	3,4	360	0,15	18,9	57,2	7900	188	0,04	37,1	37,5
7	3,9	45	0,02	6,5	5,0	4500	130	0,01	25,1	11,5
8	4,4	760	0,23	17,7	38,4	13900	435	0,19	29,8	32,4
9	7,5	570	0,37	16,9	60,0	13500	474	0,07	42,2	76,2
10	7,8	354	0,08	28,4	29,9	15600	485	0,03	14,3	52,1
MPC (mg/kg)	2,0	200-350	1,0	6,0	3,0		1500	2,1	6,0	23
BC (mg/kg)	15		3	40	100		250	0,4	20	70

As can be seen from the Table, in many sites the concentrations of some heavy metals, especially As, Ba, Cr, Cu, Pb and Zn were found to be greater than their permissible levels accepted in the republic. The contents of most toxic metals like As, Pb and Zn ranged from 3,4 to 8,2 mg/kg, 14,3 to 42,2 mg/kg and 11,5 to 105 mg/kg, respectively. In several sites, their values exceeded the background levels to some extent. However, no exceeding of maximum permissible and background values on Hg, Cd and Mn was detected in soil during the studies.

According to their effects on the environment, majority of the studied metals fall within the following categories, except Fe which has low toxicity:

1. As, Hg, Pb, Cd and Zn – super dangerous
2. Cr and Cu – dangerous
3. Ba and Mn – moderate dangerous

The results of microbiological studies have shown that biological activity of oil contaminated soils is strongly depending on their contamination degree. Major part of soil in the territory of oil and gas fields is characterized by suppression of biological activity. Petroleum hydrocarbons are technogenic wastes, in which the processes of natural self-purification capacity substantially weakened (Kolesnikov et al., 2010; Leahy and Colwell, 1990). Different subtypes of gray-brown soils were used to determine the microbiological quality of soils. As can be seen from Table 3, all samples containing small amounts of hydrocarbons have high microbial activity. Sample 2 was accepted as background during the studies. In uncontaminated soils, microbiological processes intensity varies depending on their physico-chemical properties. In the soils characterized by natural moisture, microbiological processes proceed more intense compared to those, in which geothermal factor is less favorable. The arid climate is one of the key factors limiting microbiological degradation of hydrocarbons in the Absheron soils. Despite the fact that during sample collection direct field studies showed low moisture content in soils, however even in these conditions they are characterized by relatively high microbiological activity due to the presence of microorganisms adapted to the arid environmental conditions. They constituted high numbers of saprophytes (microorganisms capable of degrading organic substances) and hydrocarbon-oxidizing microorganisms. Uncontaminated soils of the study are a differ from oil-contaminated soils with high mineralization coefficients indicating that these soils have self-purification capacity, incase if the degree of hydrocarbon concentrations does not suppress the activity of soil microorganisms.

Complete suppression of microbiological degradation of hydrocarbons in highly contaminated areas is explained by hard saturation of soils with heavy oil fractions–asphaltenes and tars that prevent the diffusion of atmospheric oxygen and also by the absence of nitrogen, phosphorus and other biogenic elements that are necessary for microbial activity.

Table 3. Microbiological activity of soils depending on the degree of oil contamination

Soil samples	Content of oil,%	Respiration intensity, CO_2 , mg/kg Soil	Number of h/carbons[2] oxidizing m/org[3]., per 1g of soil	Number of heterotrophic m/org., per 1 g of soil	Coefficient of mineralization, C_m
1	0,0015	1,93	$5{,}9{\cdot}10^8$	$5{,}3{\cdot}10^8$	1,73
2	0,002	3,6	$8{\cdot}10^8$	$4{\cdot}10^8$	1,8
3	0,004	3,5	$7{,}9{\cdot}10^8$	$3{,}9{\cdot}10^8$	1,7
4	0,05	2,1	$4{,}9{\cdot}10^8$	$5{,}8{\cdot}10^7$	0,25
5	0,97	0,5	$4.5x10^2$	ND[1]	0,06
6	10,7	ND	ND	ND	ND
7	21,4	ND	ND	ND	ND

Note: 1. ND-not detected or below instrumental direction limits; 2. h/carbons-hydrocarbons; 3. m/org.-microorganisms.

The results derived from the current study demonstrated that:

1. As a result of long-term production, transportation and processing of hydrocarbon resources the oil contamination degree of soils in the territory of oil fields of the Absheron peninsula is very high and reaches 22%. The depth of soil contamination with oil predominantly reaches 1,5m and in some cases, even deeper.

2. The oil contaminated soils contain considerable quantity of PAH, asphaltenes, and highly toxic heavy metals including As, Pb and Zn, which concentrations exceed maximum permissible and background levels.

3. The results of researches showed that oil contamination significantly influences microbiological conditions of soils. Hydrocarbon-oxidizing microorganisms are absent in the oil contaminated soils. Very low values of mineralization coefficients indicate that these soils are not capable of natural biological self-purification.

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