

Transformation of Polycyclic Aromatic Hydrocarbons at Degradation of Petroleum in Soil

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Abstract: The content of oil, tar and asphaltene fractions in crude and degraded in soil petroleum from Surakhani oil fields of Absheron has been determined. The regularities of distribution of polycyclic aromatic hydrocarbons (PAH) in oil and tar fractions of crude and degraded in soil petroleum have been studied. Three groups of PAH – containing 2-6 benzene rings, NPD (Naphthalene, Phenanthrene-Dibenzo(ah)anthracene) and 16 EPA have been considered. It is shown that within the transition from oil fraction to tar the content of 2-6 PAH increases by 45%, 16 EPA – by 33.6% and NPD – by 38,5%. Besides the sharply increase of the content of the asphaltene fraction within the degradation of oil in soil, the content of the identified PAH decreases both in oil and tar fractions.

Key words: petroleum, soil, degradation, PAC

1. Introduction

The most resistant to the effects of microorganisms and other environmental factors among the components of oil are PAHs because of toxic exposure and insolubility in water. On one hand, the insolubility in water reduces the probability or prevents the ingress of PAH in living organisms; on the other hand, it leads to their accumulation in the environment, for example in the bottom sediments of reservoirs. The influence of light and ionizing radiation, pH, mineral water environment, presence of humic acids in soil, etc. affect their transformation in the environment [1-3]. Degradation processes for Azerbaijan oil have been studied in the example of Balakhani oil-fields [4-5]. However, the issues related to the transformation of polycyclic aromatic hydrocarbons within oil degradation have been considered partly [6], detailed studies have not been conducted.

The research results of transformation of PAH during petroleum degradation in soil of Surakhani oil field of Absheron have been presented in the paper.

2. Methodology

For comparison, the oil samples were taken both from the contaminated soil and freshly produced from well. After purification from impurities, the oil samples were divided into three fractions: oil, tar and asphaltenes (Table 1) according to GOST 1158-66.

The asphaltene content in the oil composition turned out insignificant, and the study of PAH was carried out in oil and tar fractions of the petroleum.

For analyzing the products in liquid phase, it was used GC-mass spectrometric method. Chromatograph GCFID (GS-450, Varian-2010 USA) and mass-spectrometer GC/MS Trace DSQ (Thermo Electron, Finnigan USA, 2005) were used.

Table 1 Fractional composition (wt %) of oil samples taken from well and soil.

Sample	oil	tar	asphaltenes
Oil from soil	71.1	22.4	6.5
Oil from well	90.9	9.0	0.1




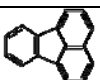


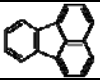
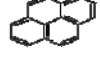
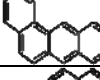
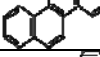
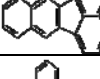
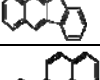
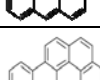
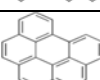


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The oil samples were dried with dry Na_2SO_4 , and then diluted with dichloromethane (CH_2Cl_2) for chromatographic analysis. The analyses were performed on the device GC/MS Trace DSQ (Thermo Electron, Finnigan USA, 2005) within the range of $m/z = 35\text{--}400$ (m/z -mass to charge ratio), and the components in the products were identified on the base of mass-spectra.

3. Results and Discussion

Because the polycyclic compounds are the most toxic from the ecological point of view, the study of their changes during oil degradation processes in the environment is of interest. Table 2 presents the main characteristics of PAH, which are the subject of these studies.

Table 2 The main characteristics of 16EPA PAH in the oil fraction.

16EPA -PAH	M, g/mol	Chemical structure	Chemical formula	Number Ring, k	Toxic e Toxic equivalency factor
Naphthalene	128		C_{10}H_8	2	0.001
Acenaphthylene	152.2		C_{12}H_8	3	0.001
Acenaphthene	154.2		$\text{C}_{10}\text{H}_{10}$	3	0.001
Fluorene	166.2		$\text{C}_{13}\text{H}_{10}$	4	0.001
Phenanthrene	178.23		$\text{C}_{14}\text{H}_{10}$	3	0.001
Anthracene	178.23		$\text{C}_{14}\text{H}_{10}$	3	0.01
Fluoranthene	202.26		$\text{C}_{16}\text{H}_{10}$	4	0.001
Pyrene	202.26		$\text{C}_{16}\text{H}_{10}$	4	0.001
Benzo(a)anthracene	228.29		$\text{C}_{18}\text{H}_{12}$	4	0.1
Chrysene	228.29		$\text{C}_{18}\text{H}_{12}$	4	0.01
Benzo(k)fluoranthene	252.32		$\text{C}_{20}\text{H}_{12}$	5	0.1
Benzo(b)fluoranthene	252.32		$\text{C}_{20}\text{H}_{12}$	5	0.1
Benzo(a)pyrene	252.3		$\text{C}_{20}\text{H}_{12}$	5	1
Indeno(123cd)pyrene	276.3		$\text{C}_{22}\text{H}_{12}$	6	0.1
Benzo(ghi)perylene	276.3		$\text{C}_{22}\text{H}_{12}$	6	1
Dibenzo(ah)anthracene	278.3		$\text{C}_{22}\text{H}_{14}$	5	5

As can be seen from the table, the toxicity of the individual PAHs (especially benzo-compounds) exceeds others' toxicity a thousand times. Therefore, the mutual transformations of these PAHs are reasonable from the ecological point of view, and the study of these processes under different factors is of great practical and scientific interest.

It should be mentioned that the presence of all three groups of PAH exceeds their values in the tar fractions of both crude and degraded in soil petroleum in comparison with the oil fractions. Thus, in the tar fraction of crude oil the content of 2-6 PAH is 45%, 16 EPA 33.6% and NPD 38.5% higher than in the oil fraction. For example, for Fluorene and Phenanthrene this difference is 2.5 times, but for Anthracene and Fluoranthene almost 5 times. There is a growth tendency also in the content of the above-shown hydrocarbon groups with an increase in the molecular weight of PAH and number of benzene rings in their composition. Only naphthalene content in the oil fraction is 47% higher than in the tar fraction. These patterns are most probably associated with the specific formation processes of different compound groups within the genesis and metamorphism of petroleum.

We have studied the class of PAH 16 EPA in more detail. The dependence of the ratio of the concentrations of the individual PAH in tar (Ct) and oil (Co) fractions on their molecular weight and number of aromatic rings (k) is given in Fig. 1. The figure shows that with an increase in both of these values the

Ct/Co ratio increases. Moreover, this value in the crude oil grows faster than in the degraded one, and at $k > 3$ this ratio becomes 2.5 times greater than in the degraded oil. In degraded oil, this ratio does not exceed 4 at all values of k .

Within the oil degradation in soil the PAH content decreases both in oil and tar fractions. The decrease in 2-6 PAH rings amounts to 33.5% for oil and 49.8% for tar fraction. The appropriate numbers for NPD are 34.5% and 49.4%, and for 16 EPA 48.8% and 43.2%. As it is seen from Table 1, in the oil degradation process the asphaltene content increases from 0.1% to 6.5%, i.e., 65 times in its composition. Apparently, the reduction in PAH in the composition of oil and tar is associated with the fact that the heavy part of oil hydrocarbons polycondenses and separated into asphaltenes. In addition, our methodology does not determine the PAH with benzene rings of which number is more than 6. Moreover, the greater the molecular weight and number of aromatic weight, the more quickly the polycondensation process occurs than in light PAH. In Figs. 1 and 2, it is shown the dependence of the ratio of the individual PAH concentrations in the composition of oil and tar fraction of the original and degraded oil on the number of benzene rings and molecular weight. It is seen that with increase of the number of rings and molecular weight the ratio of Ct/Coil increases, which indicates the behavior of polycondensation processes. In this case, these processes occur more quickly in oil fraction and the content of PAH decreases in lighter oil fractions. On the other hand, PAH are more soluble in water at smaller amounts of aromatic rings and accordingly, they are subjected significantly to biodegradation by microorganisms. Salt and humus content in soil also affects the dissolution process positively. Thus, a sharp decay in the curves of Fig. 2, is apparently related to a higher rate of degradation of relatively light ($k < 4$) PAH than heavy ones. Moreover, it should be also considered the role of direct and indirect photochemical decay of PAH under solar radiation.

Table 3 Content of various PAH groups in the composition of oil and tar fractions of the crude and degraded oil (mg/kg).

Oil fractions	A total of PAH with 2-6 benzene rings	NPD	Total - 16EPA
Oil of crude petroleum (yq)	14016	13652	962
Oil of degraded petroleum (yt)	9308	8936	492
Tar of crude petroleum (qq)	20375	18912	1286
Tar of degraded petroleum (qt)	10224	9567	730

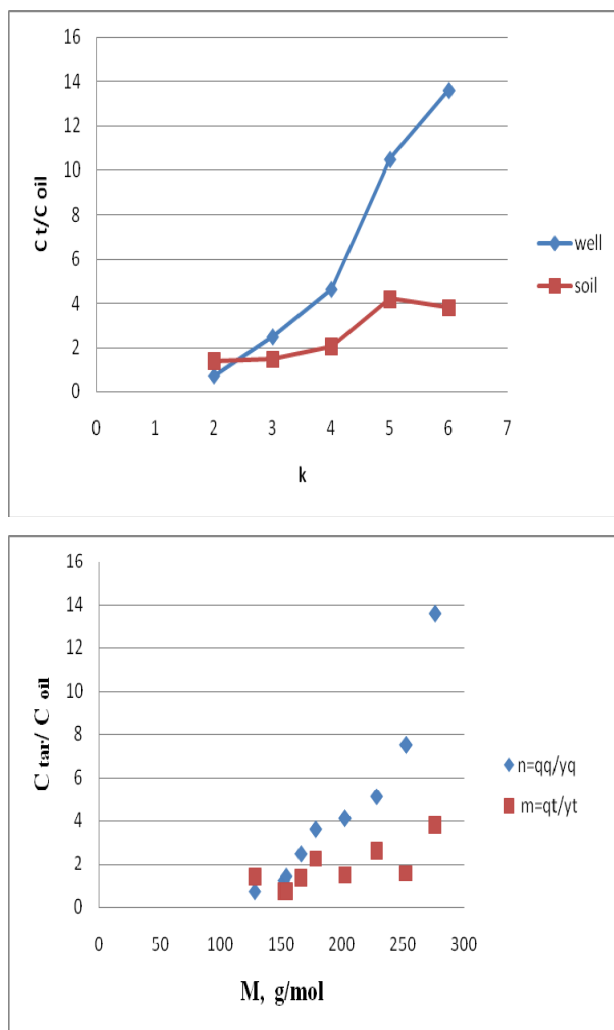


Fig. 1 Dependence of the ratio of the individual PAH content in oil and tar fractions of the crude and degraded oil on the number of benzene rings and molecular weight.

For all groups of PAH there is a reduction in their content within the degradation of oil in soil. This relates to the measurable PAH in the oil composition.

It should be noted that our analytical methodology identifies only the PAH with aromatic units up to 6. Therefore, reduction in the content of these PAH groups is apparently related to the polycondensation of PAH with aromatic nuclei less than 6, and the formation of heavier PAH which we are not able to identify. Since the asphaltene content sharply increases in the degradation process, it can be assumed that a part of PAH segregates together with the asphaltenes.

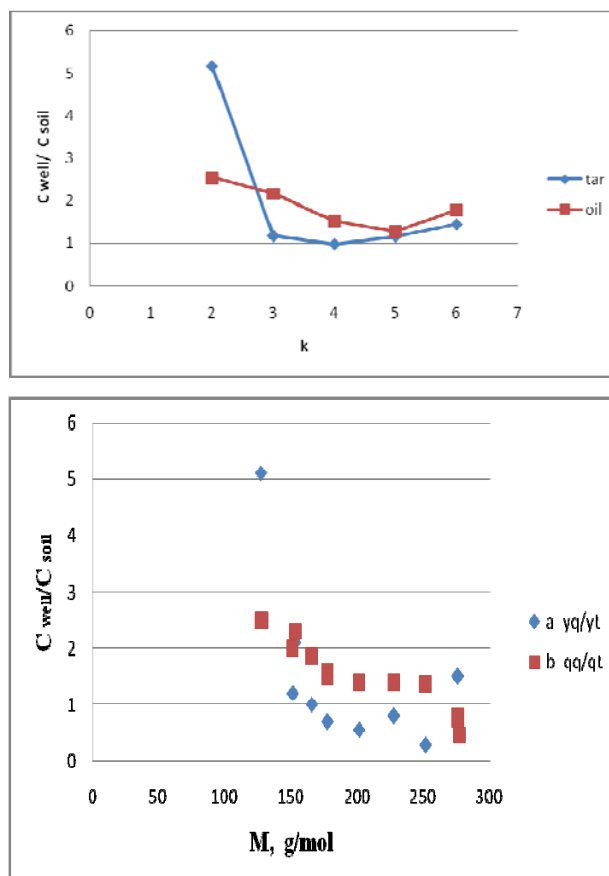


Fig. 2 Dependence of the ratio of the individual PAH content in oil and tar fractions of the crude and degraded oil on the number of benzene rings and molecular weight.

4. Conclusion

(1) The ratio of individual PAH content in oil and tar fractions of oil (n) strongly depends on the number of benzene rings, and reaches up to 13.6 at $k=6$ in crude oil. This dependence in degraded oil in soil gets relatively weak character, and the value n does not exceed 4 at $k=5-6$.

(2) Within the degradation of oil in soil the content of light PAH is strongly transformed both in the oil and tar, the content of relatively heavy PAH with $k=4-6$ changes only 1.5-2 times. Reduction in PAH content in degradation process is likely due to the destructive and polycondensation processes.

References

- [1] F. Valerio and A. Lazzarotto, Photochemical degradation of polycyclic aromatic hydrocarbons (PAH) in real and laboratory conditions, *International Journal of*

- Environmental Analytical Chemistry* 23 (1985) 1-2, 135-151.
- [2] L. Desiree Plata, Charlesm Sharpless and Christopherr Reddy, Photochemical degradation of polycyclic aromatic hydrocarbons in oil films, *Environ. Sci. Technol.* 42 (2008) 2432-2438.
- [3] Environmental Degradation of petroleum hydrocarbons, by R. M. van der Heul Utrecht University/IRAS, 3061655, November 2009.
- [4] I. Mustafayev, K. Yakubov and N. Guliyeva, Radiation-chemical transformations of oil degraded on water surface and in the soil, *5th Eurasian Conference on Nuclear Sciences and Applications*, Ankara, Türkiye, Oct. 2008, pp. 164-165, 14-17.
- [5] I. I. Mustafayev, A. P. Mammadov, S. F. Aliyeva and R. A. Jafarova, Degradation of absheron oil in the environment, *Ecology of Industrial Production* 1 (85) (2014).
- [6] N. Guliyeva, I. Mustafayev, S. Mamedova and S. Aliyeva, Radiation resistance of tar fractions of bituminous oil, *J. Chemistry and Chemical Engineering* 9 (2015) 357-362.