PETROLEUM FRACTIONS DISTRIBUTION IN A CRUDE OIL POLLUTED SOIL FROM BRAILA COUNTY

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Abstract: *Romania still depends largely on crude oil for income earnings. Crude oil spillage is also a very common problem in the country. There is therefore a need for continuous research on the problems associated with pollution resulting from spillage and its effects on the soil environment which has a negative impact on crop growth on it. There are a variety of pollutants affecting soil and subsoil, such as fuel and oil products, hydrocarbon residues, crude oil, other products resulting from the operation (saturated and unsaturated aliphatic hydrocarbons, and the monocyclic and polycyclic aromatic). These types of products (mainly hydrocarbons) have a harmful risk, affecting the quality of groundwater, which becomes unfit for use for a long time (drinking water, irrigation and different industrial uses). It also poses risks to human health, biological environment and vegetation, aromatic compounds having a strong feature of mutagenic and carcinogenic and, not least, affect the environment security, presenting risks of explosion and fire, when the floating oil reach the groundwater in the basement of various buildings. The case study was achieved at Perisoru, Braila county, in an area polluted by crude oil criminal drilling in a transport pipeline. This study includes: presentation of the area, the main morphological features, physical, agrochemical and microbiological characteristics of soil samples collected from polluted area and the soil profile of the maximum pollution compared with those of uncontaminated soil in the vicinity of the polluted area, the dynamics of pollutant migration depth of soil profile horizons depending on the sequence and genetic characteristics and the degree of pollutant loading. The paper presents the results obtained for petroleum fractions in soil samples polluted with crude oil. The conclusion of the case study investigated in the crude oil polluted area was that the physico-chemical and biological characteristics make chernozem a good environment for biodegradation process, if they occur in order to optimize the factors that control the bioremediation process. Without the application of pedo-ameliorative measures to stimulate biodegradation and specific return as state of land before the pollution occurrence, would occur very slowly, self-cleaning process requiring unacceptable periods of time.*

Key words**:** *crude oil, case study, Braila county, petroleum fractions, polluted soil*.

INTRODUCTION

The release of crude oil into the environment by crude oil spills is receiving worldwide attention. Petroleum fuel and crude oil products represent the one of the most common environmental contaminant. Common sources of these products are motor fuel station underground storage tanks, home and commercial heating oil storage tanks, fuel distribution centers, refineries, crude oil production sites and accidental spills (BURGER, 1993; BURNS ET ALL, 1993; PEPPER, 1997).

Most crude oil pollution sources are anthropogenic, but there are also some natural sources. There is evidenced that some organisms, such as high-class plants are able to synthesize hydrocarbons and can penetrate the soil. Crude oil is a complex mixture of hydrocarbons. It includes aliphatic hydrocarbons, aromatic hydrocarbons, asphaltenes and resins.

These types of products (mainly hydrocarbons) have a harmful risk, affecting the quality of groundwater, which becomes unfit for use for a long time (drinking water, irrigation

and different industrial uses). It also poses risks to human health, biological environment and vegetation, aromatic compounds having a strong feature of mutagenic and carcinogenic and, not least, affect the environment security, presenting risks of explosion and fire, when the floating oil reach the groundwater in the basement of various buildings (BURNS ET ALL, 1993).

MATERIALS AND METHOD

The degree of pollution with crude oil in the studied area has been established achieving a case study in Braila county. This area is known as having a historical pollution with petroleum hydrocarbons (GASTESCU AND GRUESCU, 1973). Perisoru, part of Braila county is located on the map at 45°7' North 27°29' East.

The perimeter in which has been achieved the case study was chosen according to the massive pollution of cracking a crude oil pipeline. Crude oil spilled in different proportions affected soil until 120 cm and 3 soundings until 60 cm, except S1 where it goes until 90 cm. The profile P1, S1 and S3 soundings were classified as epicalcaric chernozem and S2 sounding as proxicalcaric chernozem according to the Romanian System of Soil Taxonomy (FLOREA AND MUNTEANU, 2003).

For total petroleum hydrocarbons and petroleum fraction determination was used gravimetric method.

RESULTS AND DISCUSSION

Crude oil provided by transport pipelines have led to soil cover with a film, which the stay to its surface and formed a crust. At soil surface remained asphaltenes forming crust, and the other hydrocarbons with a lower molecular weight penetrated and completely obstruct the soil pores causing air traffic stop. Lack of oxygen involves stopping the biodegradation process of petroleum hydrocarbons.

This phenomenon, comparable to animal bodies hypoxia (lack of oxygen to cells) led to the installation of an anaerobic system in soil, leading to faster or slower death forced aerobic microorganisms and cells root, with the consequent inability of roots to retrieve sap and support plant metabolism (figure 1).

The concentration of total petroleum hydrocarbons (TPH) were determined in soil samples taken from the area under study. The classification of obtained results from loading degree point of view was made in accordance with the classification scale (Toti et all., 1999).

In the profile achieved in Perisoru area, Braila County was registered a very strong pollution with petroleum hydrocarbons, a descending pollution. In Amt horizon, 0-20 cm was registered a concentration of total petroleum hydrocarbons by 92000 mg/kg, in Am horizon at 20-40 cm depth, the concentration has a value of 82400 mg/kg. The Ac1 horizon located at a depth of 55-75 cm there is a halving of total petroleum concentration with a value by 41700 mg/kg, almost identical to that of AC2 horizon located at 75-95 cm depth with a value by 41000 mg/kg. At 100-120 cm depth was identified last horizon of the profile and value of total petroleum content in continued to decrease reaching the value 32100 mg/kg, which maintains the level of excessive pollution. The evolution of total petroleum concentration with horizon in the profile achieved at perisoru, Braila County.

In the sounding 1 (S1) made on 4 depths was registered the highest concentration of total petroleum hydrocarbons with a value by 50300 mg/kg on 20-40 cm depth, followed by 43400 mg/kg on 70-90 cm depth, 19700 mg/kg at surface (0-20 cm) and 12000 mg/kg on 50-70 cm depth. Sounding 2 (S2) have been realized on 3 depths, being registered a decrease in total petroleum hydrocarbons content with depth. Thus, there was a surface concentration of total petroleum hydrocarbons by 33200 mg/kg, 40200 mg/kg on 20-40 cm depth, and 18000 mg/kg on 40-60 cm depth. The concentration of total petroleum hydrocarbons in sounding 3

(S3) presents in the first horizons a descending pollution from 20400 mg/kg at the surface drops to 13900 mg/kg at a depth of 20-40 cm and then a strong ascending pollution concentration reaching the value of 57400 mg/kg.

After three months, the concentration of total petroleum hydrocarbons decreased, but, the pollution is still strong in mainly as it can be observed in table 1.

Table 1

Concentration of total petroleum hydrocarbons (TPH) and oil fractions in soil sampled from the polluted area three months after the second sampling

No.	**Location**	**Depth cm**	**TPH** (mg/kg)	
			First sampling	Second sampling (after three months)
1	Perişoru Ianca, Profile 1	0-20	92000	47700
2		20-40	82400	34650
3	Perişoru Ianca, S1	0-20	19700	nd
4		20-40	50300	150
5	Perişoru Ianca, S2	0-20	33200	14500
6		20-40	40200	43550
7	Perişoru Ianca, S3	0-20	20400	27200
8		20-40	13900	28650

Figure 1 Image presenting soil cover with an asphaltenes film from crude oil

Table 2

Concentration of total petroleum hydrocarbons (TPH) and oil fractions in soil sampled from the polluted area three months after the second sampling

No.	Location	Depth cm	TPH		Petroleum fractions distribution							
					Aliphatic Hydrocarbons		Aromatic Hydrocarbons		Resins		Asphaltenes	
			%	mg/kg	%	% from TPH	%	% from TPH	%	% from TPH	%	% from TPH
1	Perişoru Ianca, Profile 1	0-20	4,77	47700	2,23	46,75	0,98	20,55	1,11	23,27	0,29	6,08
2		20-40	3,47	34650	2,28	65,71	0,57	16,43	0,50	14,41	0,10	2,88
3	Perişoru Ianca, S1	0-20	nd	nd	na	na	na	na	na	na	na	na
4		20-40	0,01	150	na	na	na	na	na	na	na	na
5	Perişoru Ianca, S2	0-20	1,45	14500	0,47	32,41	0,41	28,28	0,41	28,28	0,11	7,59
6		20-40	4,36	43550	0,85	19,50	1,52	34,86	1,32	30,27	0,41	9,40
7	Perişoru Ianca, S3	0-20	2,72	27200	1,49	54,78	0,64	23,53	0,45	16,54	0,14	5,15
8		20-40	2,87	28650	1,79	62,37	0,53	18,47	0,43	14,98	0,11	3,83

To observe the predominance of existing petroleum hydrocarbon fractions have been achieved fractionation of crude oil. Thus, it was observed that aliphatic hydrocarbons in profile have a clear preponderance (46.75 % in 0-20 cm depth and 65.71 % in the 20-40 cm depth). Resins and aromatic hydrocarbons are approximately equal. Regarding asphaltenes is found a higher content at soil surface (6.08 %) and lower in depth 20-40 cm (2.88 %) as it can be observed in figure 2 and 3. This explains the existence of the crust.

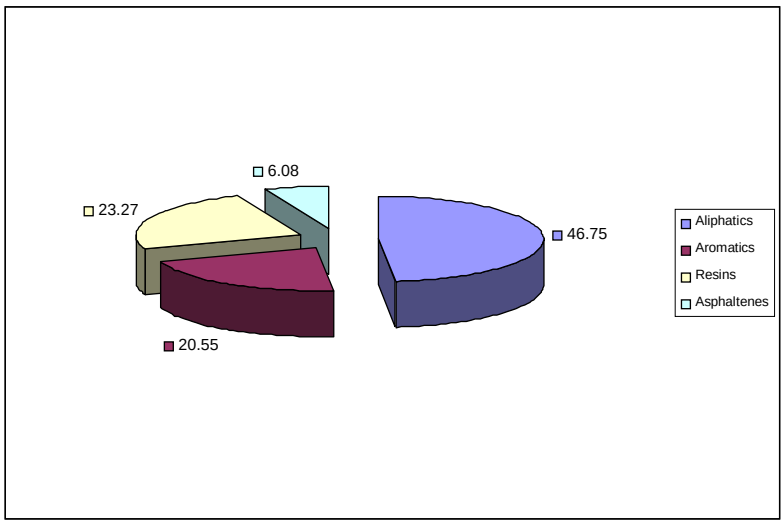

Figure 2 The content of petroleum fractions on the profile surface (Amt horizon) achieved at Perisoru, Braila County

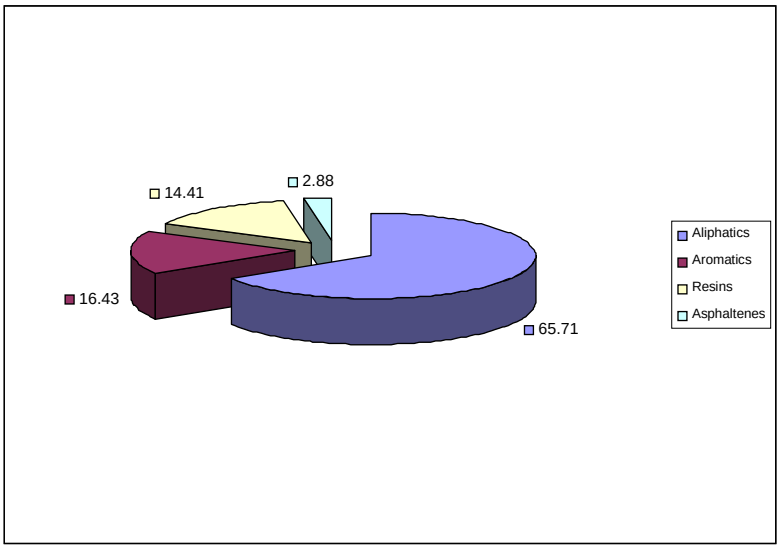

Figure 3 The content of petroleum fractions on Am horizon achieved at Perisoru, Braila County

The sounding S1 presents the lowest total petroleum hydrocarbons, being undetectable at the second sampling. The sounding S2 have aliphatic and aromatic hydrocarbons, resins rather close in values ranging from about 20-30 % , on the other hand are high asphaltenes content of 7.59 % in a depth of 0-20 cm in depth and 9.40 % 20-40 cm. This is due to the contribution of crude oil that seeps into the mix fractions also left that still grow by asphaltenes concentration. S3 sounding have a higher aliphatic hydrocarbons other content gradually decreasing.

Finally after two samplings in an area polluted with crude oil can be seen that without anthropogenic intervention, without the application of specific technologies for biodegradation and improves soil quality hard time being a function of pedogenetical factors (geomorphology, climate and hydrology) depending on the movement of the pollutant in the soil depending on the composition of the natural climate and variations thereof which may enhance or inhibit the action of microorganisms in soil.

CONCLUSIONS

The case study was achieved in an area known for the history of petroleum hydrocarbons pollution. The pollution degree of the studied area is excessive in the majority of the soil samples. In the profile achieved in Perisoru area, Braila County was registered a very strong pollution with petroleum hydrocarbons, a descending pollution. In the sounding 1 (S1) made on 4 depths was registered the highest concentration of total petroleum hydrocarbons on 20-40 cm depth and on 70-90 cm depth. Sounding 2 (S2) have been realized on 3 depths, being registered a decrease in total petroleum hydrocarbons content with depth. In sounding 3 (S3) in the first horizons a descending pollution and then a strong ascending pollution concentration. It was observed that aliphatic hydrocarbons have a clear preponderance. Resins and aromatic hydrocarbons are approximately equal. Regarding asphaltenes is found a higher content at soil surface and lower in depth.

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