THE EFFECTS OF CRUDE OIL POLLUTION ON PHYSICAL AND CHEMICAL CHARACTERISTICS OF SOIL

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Abstract: *Pollution caused by crude oil is the most prevalent problem in the environment. The release of crude oil into the environment by oil spills is receiving worldwide attention. Crude oil products represent the one of the most common environmental contaminant / pollutant. Most oil pollution sources are anthropogenic, but there are also some natural sources. 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. There is evidenced that some organisms, such as high-class plants are able to degrade hydrocarbons and can penetrate the soil. Crude oil is a complex mixture of hydrocarbons. It includes an aliphatic fraction, an aromatic fraction, asphaltenes, and resins. The effect of crude oil pollution on physical and chemical characteristics of soil was investigated by achieving a case study in Perisoru, Braila County. It has been achieved a profile until 120 cm and 3 soundings until 60 cm from where soil samples were collected according to the methodology and analyzed for physical and chemical characteristics point of view. In case of physical analysis, the values obtained for granulometric fractions were not influenced by the presence of crude oil. Results obtained showed variation in chemical properties of soil. Organic carbon increased from 2.23% for an unpolluted soil to 5.51% in polluted soil. C/N ratios increased from 13 for an unpolluted soil to 21 in polluted soil. Mobile phosphorous and potassium registered in polluted soil similar values with the one characteristic for unpolluted soil. Crude oil at high pollution levels inhibited the growth of crops. Because high concentrations (>1%) of petroleum hydrocarbons in soil have demonstrated phytotoxic properties, as well as the uncertainty about the fate and transport of high concentrations of petroleum in soils and upon human health, the specific fuel nondefault closure levels have maximum limits applied. It is generally recognized that the toxicity, (human and environmental), of petroleum products increases as the molecular weights of the compounds decrease.*

Key words**:** *crude oil, pollution, physical and chemical characteristics of soil, Braila County.*

INTRODUCTION

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. Hence this particular study had as its main objective to examine the effects of crude oil on soil physical and chemical properties (GÂȘTESCU and GRUESCU, 1973; TOTI et al., 1999).

Soil pollution is defined as the appearance in soils of persistent toxic compounds, chemicals, salts, radioactive materials, or disease causing agents, which have adverse effects on plant growth and animal health (PEPPER, 1996). One of the most important classes of organic pollutants in the environment is crude oil constituents of petrochemicals.

Accidental oil pollution has become nowadays a common phenomenon that can cause environmental and social disasters (BURGER, 1993; BURNS, 1993). Potential sources of direct pollution of soil and subsoil can be covered by tanks, separators old from wastewater treatment plants, settling basins, slurries and waste pits of tar, ramp CF loading and unloading, underground pipelines, sewerage networks, etc.

Solid residues, unstored corresponding, which can pollute the soil, come from: solid impurities involved in crude oil, sewage sludge from wastewater treatment plants and raw water treatment, solid waste from the maintenance and cleaning of incinerator ash sludge, powder catalyst (NEAG, 1997).

MATERIAL AND METHODS

The perimeter in which has been set for the case study was chosen according to the massive pollution of cracking a crude oil pipeline from CONPET. Crude oil spilled in different proportions affected soil until 120 cm and 3 soundings untill 60 cm, except S1 where it goes untill 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). In the control area were performed two soil profiles. For the characterization of soil cover in particular the upper horizon of their samples were collected in two depths (0-20 cm and 20-40 cm).

The analysis achieved using the ICPA methodology were: granulometric fractions, soil reaction by potentiometric method, organic carbon content by titrimetric method of Walkley Black, total nitrogen content by Kjeldahl method, C/N ratio by calculation, mobile phosphorus content by Egner-Riehm-Domingo method, mobile potassium content by flamephotometer method, total petroleum hidrocarbons by gravimetric method and soluble salt content by conductometric method according to the methodologies (METHODOLOGIES, 1981, 1986).

RESULTS AND DISCUSSIONS

Physical and chemical characteristics of soil samples from the studied area are presented in following tables. Physical characteristics are presented in table 1 for control area and in table 2 for polluted area. Chemical characteristics are presented in table 3 for control area and in table 4 for polluted area.

According to the results of physical analysis, all samples fall within the clay textural class. Coarse sand registered the normal values at majority depths. Fine sand shows values between 42.6% and 51.7% in case of polluted area. Dust is found more in the surface horizon with a value of 26.2% and the lowest value recorded in Ac_1 horizon, 55-75 cm, had a value of 24.2%. Clay has the highest value in the horizon of the C_{Ca} profile - 34% and the lowest in the Ac_1 horizon - 25.8%. Compared with unpolluted soil chernozem, the values of each fraction is similar with the results obtained in the polluted soil. The granulometric fractions are not influenced by the presence of crude oil.

Soil reaction is weak alkaline in all the samples ranging between 7.70 to 8.26, except for samples taken from Amt horizon, the depth of 0-20 cm, showing a weak acid reaction (6.22) and samples taken from Am horizon, the depth of 20-40 cm, which shows a neutral reaction (6.83).

If an unpolluted soil contain organic carbon from 2.23% to 2.02% in the first horizons 0-20 cm and 20-40 cm depth, the values obtained in the polluted profile are much higher, being registered contents by 5.51%, respectively, 4.44%. Also, organic carbon contents decrease with depth reaching a value by 2.43% which indicates that oil pollution has come down to that depth. Normally at this depth, organic carbon content in an unpolluted soil would vary between 0.3-0.5% being extremely low. Crude oil has a significantly influence on this parameter, the values determined being much higher because of the presence of pollutant.

Total nitrogen content in the moderate class is falling all the samples analyzed is between 0.151% - 0.251%, except for samples taken from Amt horizon, the depth of 0-20 cm, showing a high content of total nitrogen (0.313%) and AC1 samples collected from the horizon, the depth of 55-75 cm, showing a lower total nitrogen content (0.133%). Compared to the total nitrogen content recorded in control area, the values obtained in polluted almost similar.

The C/N ratios have the same behavior as organic carbon content. If an unpolluted soil chernozem has a C/N ratio ranges between 13.01 and 12.88 in the 0-20 cm and 20-40 cm depth, in the polluted profile the values for C/N ratios are much higher ranging between 20.54-20.64. The maximum value was registered in 55-75 cm depth where it reaches a value of 30.53 and started to decrease with depth, being registered a value of 21.84 at 75-95 cm depth and a value of 16.02 at 100-120 cm depth. On all sampling depths, in the polluted area, the situation is very different, the values of C/N ratio are much higher. It also other, C/N decreases with depth reaching 16.02%, which indicates that oil pollution has come down to that depth. Normally at this depth, the C/N has values ranging from 10 to 11 indicating a small content. Thus, if the polluted area from Perisoru, high content are registered from the surface to 120 cm because of the presence of crude oil. Moreover, total petroleum hydrocarbon content will certify the values of C/N ratio and the organic carbon content increased highly comparatively with unpolluted soil because of loading with pollutants.

In the control area, the values obtained for mobile phosphorus content includes in a small content class. The content of mobile phosphorus profile decreases with depth, with high content on the surface, middle in the 2nd horizon, over the next three horizons small value indicating content. In all three surveys, this parameter decreases with depth. In the polluted profile, mobile phosphorus content decreases with depth, reaching a maximum value at the surface. In the second horizon, the mobile phosphorous decreases by half, over the next three horizons is constant value representing only 1/7 of the value registered on the surface. Thus, in Amt horizon (0-20 cm) of profile was determined a value by 73 mg kg^{-1} which indicates a high content of mobile phosphorus on the surface. The value registered at the surface drops to half in the Am horizon located on 20-40 cm depth having a value by 36 mg kg^{-1} which indicates middle mobile phosphorus content. In the Ac_1 horizon (55-75 cm), in the Ac_2 horizon (75-95 cm) and in the C_{Ca} horizon (100-120 cm) was determined lower content of mobile phosphorus values by 11 mg kg^{-1}, 11 mg kg^{-1}, respectively 8.73 mg kg^{-1}. Compared to the contents of mobile phosphorus recorded in an unpolluted soil, the values in the study area are higher, but not significantly because some doses distributed CONPET which content phosphorus and other absorbent materials to remedy the situation.

Mobile potassium contents obtained in the control area are similar to the values from polluted area. The mobile phosphorus content decreases with depth, having a maximum value at the surface, decreases by half in the other four horizons. Thus, Amt horizon at 0-20 cm depth was determined a value of 222 mg kg^{-1} which indicates a high content of mobile potassium on the surface. The values recorded in the Am horizon located at a depth of 20-40 cm and Ac_1 horizon at 55-75 cm falls within the middle class having a value by 112 mg kg^{-1} in both horizons. In the Ac_2 horizon (75-95 cm) and C_{Ca} horizon (100-120 cm) were determined low potassium content being registered a value by 96 mg kg^{-1} and 80 mg kg^{-1}. In case of potassium, the situation is similar with phosphorous, so compared to the contents of mobile potassium recorded in an unpolluted soil, the values in the study area are higher, but not significantly because some doses distributed CONPET which content potassium and other absorbent materials to remedy the situation.

Tabel 1

Physical characteristics of soil sampled from control area located in Perisoru, Braila County

No.	Control profile	Soil type and subtype	Depth cm	Granulometric fractions (mm) (%from mineral part of soil)				Carbonates %	Symbol Textural class
				Coarse sand 2,0-0,2	Fine sand 0,2-0,02	Dust 0,02-0,002	Clay <0,02		
1	Control profile - P1	Epicalcaric cernozem	0-20	0,2	44,7	24,3	30,8	0,0	LL
2			20-40	0,3	43,9	31,4	24,4	0,0	LL
3	Control profile - P2	Proxicalcaric cernozem	0-20	0,1	46,3	29,5	24,1	3,1	LL
4			20-40	0,1	56,4	20,3	23,2	4,2	LL

Tabel 2

Physical characteristics of soil sampled from polluted area located in Perisoru, Braila County

No.	Location	Horizon	Depth cm	Granulometric fractions (mm) (% from mineral part of soil)				Carbonates %	Symbol Textural class
				Coarse sand 2,0-0,2	Fine sand 0,2-0,02	Dust 0,02-0,002	Clay <0,02		
1	Perişoru, Braila County, Profile 1 – P1	Amt	0-20	0,1	42,6	26,2	31,1	0,0	LL
2		Am	20-40	0,1	45,2	24,9	29,8	0,0	LL
3		AC_1	55-75	0,1	45,7	25,2	29,0	4,1	LL
4		AC_2	75-95	0,1	49,9	24,2	25,8	9,5	LL
5		C_{Ca}	100-120	0,1	50,4	25,5	24,0	13,8	LL
6	Perişoru, Braila County, Sounding – S1		0-20	0,6	51,7	24,4	23,3	9,9	LL
7			20-40	0,1	47,2	21,9	30,8	0,0	LL
8			50-70	0,2	48,9	24,5	26,4	5,4	LL
9			70-90	0,0	46,7	25,2	28,1	2,3	LL
10	Perişoru, Braila County, Sounding – S2		0-20	0,1	50,0	26,6	23,3	9,0	LL
11			20-40	0,1	49,5	25,0	25,4	5,2	LL
12			40-60	0,1	47,6	27,5	24,8	4,6	LL
13	Perişoru, Braila County, Sounding – S3		0-20	0,1	50,6	22,2	27,1	2,3	LL
14			20-40	0,1	51,1	23,0	25,8	2,5	LL
15			40-60	0,1	45,2	25,3	29,4	0,0	LL

Tabel 3

Chemical characteristics of soil sampled from control area located in Perisoru, Braila County

No.	Control profile	Soil type and subtype	Depth -cm-	pH	Organic C %	Total N %	C/N Ratio	P mg kg^{-1}	K mg kg^{-1}
1	Control profile - P1	Epicalcaric cernozem	0 – 20	6,80	2,23	0,200	13,01	3,2	206
2			20 – 40	6,79	2,02	0,183	12,88	4,1	145
3	Control profile - P2	Proxicalcaric cernozem	0 – 20	8,05	1,91	0,162	13,75	3,0	210
4			20 – 40	8,20	1,64	0,157	12,19	4,0	136

Tabel 4

Chemical characteristics of soil sampled from polluted area located in Perisoru, Braila County

No.	Location	Depth -cm-	pH	Organic C %	Total N %	C/N Ratio	P mg kg^{-1}	K mg kg^{-1}
1	Perişoru, Braila County, Profile 1 – P1	0-20	6,22	5,51	0,313	20,54	73	222
2		20-40	6,83	4,44	0,251	20,64	36	112
3		55-75	8,01	3,48	0,133	30,53	11	112
4		75-95	8,20	3,22	0,172	21,84	11	96
5		100-120	8,36	2,43	0,177	16,02	8,73	80
6	Perişoru, Braila County, Sounding – S1	0-20	8,26	2,01	0,151	15,53	13	144
7		20-40	7,73	3,77	0,165	26,66	12	112
8		50-70	8,04	2,04	0,189	12,59	10	112
9		70-90	8,02	3,00	0,177	19,77	8,28	112
10	Perişoru, Braila County, Sounding – S2	0-20	8,16	3,08	0,177	20,30	22	144
11		20-40	8,00	2,77	0,192	16,83	21	128
12		40-60	8,02	2,30	0,162	16,56	15	128
13	Perişoru, Braila County, Sounding – S3	0-20	8,01	3,17	0,165	22,41	8,06	160
14		20-40	8,02	2,61	0,211	14,43	8,05	128
15		40-60	7,36	4,21	0,191	25,71	8,04	96

CONCLUSIONS

Results of physical and chemical analysis effectuated at the polluted soil samples from polluted profile show large differences compared to the results from an unpolluted soil profile as a result of crude oil pollution in the territory. The most affected characteristics are organic carbon content and C/N ratio.

Oil removal from the soil surface is essential in reducing anaerobic processes and the depth of penetration of the pollutant.

Calcaric chernozem has a loamy texture and a moderate organic matter and nutrients contents that make the degradation process intensively, if the main limiting factors the biodegradation of the pollutant are removed.

In conclusion, crude oil polluted area taken in study can be rehabilitated without anthropogenic intervention, without the application of specific measures biodegradation and improvement of soil quality while being very difficult depending on factors that can enhance the action of microorganisms in the soil. Ameliorative measures are recommended for reconstruction of polluted areas with crude oil.

Heavily and excessive polluted areas with petroleum hydrocarbons requires an ecological restoration of land to be made on larger areas on which to make appropriate ameliorative work.

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