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Contributions to Remediation and Ecological Reconstruction of Soils Polluted with Oil and Petroleum Products

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Abstract

This article highlights the correlation between soil analyzes (pH, reactive soil, humus content, phosphorus and potassium content, grain size diagram, permeability, total organic carbon, chlorides, phosphates, minerals, iron) performed for different soil profiles and the representative physicochemical characteristics of crude oil (density, viscosity, SARA analysis) that can influence the choice of subsequent remedial technologies for soil to be played in aside. This performed experimental study showed how organic matter, pH of soil changed due to agricultural amendments, O_2 content and iron oxides in the soil, may affect the extraction of hydrocarbons from contaminated soil.

Key words: *pedological studies, solvent, extraction, soil pollution, oil, petroleum products, analyzes*

Introduction

A number of researchers [3, 10 - 13] have studied the influence of organic matter from the soil on the process of hydrophobic hydrocarbons adsorption on the ground. Other authors [2, 7, 9] classified by origin the soil organic matter in two main groups: the first group, which contains incompletely processed organic debris (plants and animals) and the second group, which consists in humus in soil. Humic acid has a very complex structure, depending on the type of soil. Hypothetical formula of fluvic acid, according to Balnois [2] contains aliphatic and aromatic structures and other functional groups. Forest humus is characterized by a high content of fluvic acid while the plain soil is characterized by a high content of humic acid [1]. Various authors (Accardi, Ekhlon) [1, 10] have shown that natural organic matter (NOM) improves the solubility and mobility of highly hydrophobic contaminants (*polychlorinated biphenyls -PCBs*, *polycyclic aromatic hydrocarbons -PAHs*) in soil. Studies in recent years have generally shown that natural organic matter in the soil plays an important role in adsorption and hence the extraction of *hydrophobic organic compounds* (HOC) from contaminated soils with oil [4, 8].

Experimental Study

The purposes of this experimental study are to assess how soil organic matter and soil pH change due to agricultural amendments and how soil O_2 and iron oxides content can influence the extraction of hydrocarbons.

The objective of this study is to perform analyzes to establish a possible correlation between certain physical and chemical characteristics of the soil (pH, *total organic compounds -TOC*, *organic substances - OS*, Fe, O_2 and soil moisture) and the extraction of HOC from contaminated soils. The influence of organic matter on soil hydrocarbon extraction was monitored on naturally contaminated soil samples with the same type of oil, but belonging to different zones in terms of land use, namely: arable and forest land. The experiments were performed using different extraction solvents on the same soil samples. In order to measure the polar compounds content, the extractions have been carried out using the gravimetric method, in Soxhlet apparatus, with and without florisil.

Thus, the influence of organic carbon on hydrocarbons desorption and extraction efficiency with type of soil (arable, forestry) could be observed.

It is interesting to study the influence of the soil organic matter on *Total Petroleum Hydrocarbons* $C_{[TPH]}$ content because, according to the analyzes carried out on the two neighboring zones (one being less sensitive use, while other being more sensitive use), areas that were infected with the same type of oil and having the same soil texture, the difference between $C_{[TPH]}$ arable land area and forest area varied widely. It should be noted that the presence of a source of pollution is an oil pipe crossing the two neighboring zones.

By determining $C_{[TPH]}$ of agricultural soils and forest soils, the influence of agricultural practices on the extraction of hydrocarbons from oil which can alter soil pH could be determined.

Thus, to evaluate the influence of soil on $C_{[TPH]}$, soil samples from the two areas were used so that we can have a much wider range of parameters set to be investigated. For extraction of hydrocarbons different solvents were used: trichloroethylene (TCE), petroleum ether and hexane.

Sampling, Preparation and Coding of Soil Samples

The soil samples were collected according to the methodology in place so that the sampling program provided:

- the extraction of hydrocarbons in the three studied cases using solvents: TCE, petroleum ether and hexane;
- the extraction of hydrocarbons and non-polar cleaning (with and without the addition of florisil);
- the extraction on homogeneous soil samples.

For each studied area (arable and forest) representative samples were collected. The sampling had been made by a network grid (6 x 4) alignment in which a total of 24 individual samples were collected. From these samples, four average samples corresponding to each line were obtained and each average individual soil sample was analyzed. This procedure was applied to each type of soil (arable or forestry) and for each of the two depths 0-15 cm and 15-30 cm.

In Table 1, the coding of analyzed sample soils is presented.

Table 1. Coding of soil samples

Coding of set soil samples	Coding sample	Comments
A (arable)	P1a(1/2/3/4) – Total 24 samples /P2a(1/2/3/4) – Total 24samples /total number of samples= 48 samples	Index 1 refers to samples from 0 - 15cm depth. Index 2 shows samples from 15 - 30 cm depth P1ai and P2ai are individual samples taken from arable soil from two depths to determine the physical characteristics of the soil.
F (forest soil)	P1f(1/2/3/4) – Total 24 samples /P2f(1/2/3/4) – Total 24 samples /total number of samples= 48 samples	P1fi and P2fi are individual samples collected from forest soil from two depths to determine the physical characteristics of the soil.

Analysis

In this experimental study, for the soil samples taken from the two investigated areas, arable and forest area, a series of analyzes were conducted to determine the following features:

- Physical characteristics of the soil samples: moisture, grain size, permeability, porosity;
- Chemical characteristics: Total Organic Compounds (TOC), Organic Substances (OS), pH, Fe, minerals, humus;
- Saturated hydrocarbons, aromatic hydrocarbons, resins, asphaltenes (SARA) composition, density, kinematic viscosity for the crude oil that has polluted the two areas;
- Total extractable concentrations in contaminated soils defined as $C_{[A /G]}$;
- Total petroleum hydrocarbon concentration C_{THP} using different solvents.

The determination of pH was done by the electrochemical method. The determination of iron content in the soil was done by colorimetric method with orthophenanthroline and the organic substances content in soil was determined by calcination for two hours at 600° C. Permeability, porosity, and moisture content of the soil samples were carried out according to existing methods. It should be noted that the source of pollution is the oil pipe, which traverses the two studied areas, the arable land area and the forest area. The oil that was passing through the pipe was investigated by determining density, viscosity and SARA analysis.

The evaluation of hydrocarbon concentrations in the investigated soils was done by gravimetric method, with Soxhlet apparatus, using three solvents: TCE, petroleum ether and hexane. The experimental study concerning the hydrocarbons extraction was performed with and without florisil. In this case study, the following notations are being made:

- $C_{[A / G]}$ - concentration of extractable oil and grease being defined as any material by solvent extractable soil organic matrix, including both hydrocarbons and organic compounds soil. To determine the concentration C [A / G] was performed using solvent extraction conditions mentioned without realizing florisil cleaning step.
- C_{THP} -concentration of extractable petroleum hydrocarbons being defined as the hydrocarbons extracted by solvent cleaning step when applied to polar compounds.

The difference between $C_{[A /G]}$-$C_{[THP]}$, noted in this experimental study with $C_{[CP]}$, represents the concentration of polar compounds. Determining the two parameters $C_{[A /G]}$ and $C_{[THP]}$ was done by gravimetric method which is accepted for the extraction of the non-volatile and the semi-volatile hydrocarbons in the soil.

Experimental Results

The results of the analyses made for the samples collected from the pollutant tank that is pumping crude oil on the pipe passing the two investigated areas are shown in Table 2.

Table 2. Physicochemical characteristics of crude oil

Current issue	Analysis	Values obtained	Method of analysis
		Crude oil sample	
1.	Density at 20°C, g/cm^3	0.8730	ASTM D 4052
2.	Viscosity at 40 ºC, mm^2/s	4.20	ASTM D 445
	SARA, % (wt/wt) saturated hydrocarbons aromatic hydrocarbons resins asphaltenes	 55.2 38.6 2.4 3.8	ASTM D 2549

Experimental results – soil physical characteristics:

The physical characteristics of the soils in the two areas are presented in Table 3 and Table 4.

Table 3. Physical characteristics of arable land

Characteristics	0-15 cm	15-30 cm
Grain size **2.0-0.05** **0.05-0.005** **<0.005**	 26 57 17	 16 70 14
Natural Moisture, %	13.2	17.69
Porosity, %	44	41
Permeability	7.4×10^{-5}	8.7×10^{-5}

Table 4. Physical characteristics of forest land

Characteristics	0-15 cm	15-30 cm
Grain size **2.0-0.05** **0.05-0.005** **<0.005**	 16 61 23	 23 54 23
Natural moisture, %	28.29	22.49
Porosity, %	42	41
Permeability	$1,6 \times 10^{-4}$	$1,2 \times 10^{-4}$

Soil Compounds, Concentrations of Extractable Compounds $C_{[O/G]}$ and Total Petroleum Hydrocarbons Petroleum $C_{[TPH]}$

The experimental results obtained for some soil compounds for the profiles of the arable soil at the two depths are presented in Table 5 and for the forest soil in Table 6.

Tables 7 and 8 present the concentration of total extractable $C_{[O/G]}$, when extraction was performed without the cleaning stage of polar compounds with florosil, and C_{THP} when the cleaning stage of polar compounds with florosil was applied. The difference between $C_{[O/G]}$and C_{THP} represents the polar compounds concentration, C_{COP}.

Table 5. Compounds in arable soil

Characteristics	MU	0-15 cm	15-30 cm
Moisture	%	13,2	17,69
TOC	%	2,16	2,03
Organic substances	%	6,85	6,11
Minerals	%	93,15	93,89
pH	pH units	6,45	6,75
Humus	%	1,68	0,90
Iron	mg/kg	1,04	1,34

Table 6. Compounds in forest soil

Characteristics	MU	0-15 cm	15-30 cm
Moisture	%	28.29	22.49
TOC	%	5.82	4.75
Organic substances	%	14.91	13.23
Minerals	%	85.09	86.77
pH	pH units	7.57	7.33
Humus	%	2.08	1.32
Iron	mg/kg	1.99	2.53

Table 6. TPH concentration of arable soil samples

Solvent	Depth, cm	$C_{[O/G]}$ mg/kg d.s.	$C_{[THP]}$ mg/kg d.s.	$C_{[COP]}$ mg/kg d.s.
TCE	0-15	19006	16652	2354
	15-30	9879	7759	2120
Petroleum Ether	0-15	12227	10377	1870
	15-30	6280	4465	1815
Hexan	0-15	4724	2896	1828
	15-30	2657	857	1796

Table 7. TPH concentration of forest soil samples

Solvent	Depth, cm	$C_{[O/G]}$ mg/kg d.s.	$C_{[THP]}$ mg/kg d.s.	$C_{[COP]}$ mg/kg d.s.
TCE	0-15	38335	33498	4837
	15-30	33364	28603	4761
Petroleum Ether	0-15	27669	23399	4330
	15-30	23674	19394	4280
Hexan	0-15	26285	22075	4210
	15-30	17022	12822	4200

Discussion

Humidity, TOC, OS and humus contents shows higher values in the forest area. Organic carbon content of the soil is affected by soil texture, land use and vegetation. Fine textured soils tend to have a greater amount of organic matter and they store more water, versus coarse textured soils that are well ventilated and the presence of oxygen lead to a more rapid decomposition of organic matter. Agricultural works mix the land and introduce oxygen into the soil, increase soil temperature, thereby contributing to enhanced decomposition of organic matter. Grass land soils contain deep roots that break down deep. Unlike grass land soils, forest soils are generally based on the litter decomposition from the soil surface to provide organic matter.

The results obtained for the arable land show that, due to agricultural practices, the land presents a lower content of organic matter. Agricultural works introduce oxygen in the soil, thus consuming organic matter. Lower humidity of arable land is consistent with the higher oxygen content of arable land than in the forest soil.

The physical characteristics of the soil: structure, porosity, apparent density or moisture, depend on the soil works. Agricultural practices due to amendments also lead to decreases in pH due to the acid produced by chemical fertilizers applied to the soil.

The value of the hydrocarbon concentration of the soils contaminated with crude oil, contamination that occurred through accidental break of the oil pipe that crosses the two areas investigated, is higher, regardless of the type of solvent used in the forest land, although it is at a greater distance than the location of the damage.

Hydrocarbon concentration decreases with increasing sampling depth. As for soil samples taken from the arable soil as well as taken from the forest, quantified hydrocarbon concentrations are higher when TCE was used for extraction, TCE having the highest dielectric constant of all solvents used in this experimental study.

The soil that had the highest content of organic carbon also had the highest content of polar compounds. Regardless of the solvent used for extraction, the highest content of polar compounds was obtained in forest soil, decreasing with increasing of the soil sampling depths.

Conclusions

The interpretation of experimental results presented leads to the following observations:

- It is possible that the soil which has had the least organic carbon sorbs more hydrophobic organic compounds (HOC) and, due to the strong bond between the HOC and the surface of soil particles, by extraction, low concentrations of extracted hydrocarbons result;
- Humic acids and metals which may be present in the soil can adversely affect the extraction of hydrocarbons from soils polluted and thus the concentration of TPH;
- Agricultural works introduce oxygen, so the oxygen content increases and thus decreases organic matter decomposition. If the pH is lower so the contact angle of the hydrophobic organic compound adsorbed on the surface is larger and extraction efficiency of hydrocarbons in soils is low because adsorption of hydrocarbons on the land is stronger;
- Analyzes performed for the soil profiles taken from arable and forest lands showed that forest soil has more humus and organic carbon, the adsorption is weaker and the desorption with same solvent leads to a higher hydrocarbon content;
- Quantifying the differences between with and without florisil it can be said that the total extractable concentration is even greater, as the soil contains a higher amount of organic matter;
- The soil that had the highest content of organic carbon also had the highest content of polar compounds;
- The organic matter content in the soil influences the extraction of COH and thus increase C_{THP};
- A high moisture, low O_2, high percentage of TOC, SO and humus indicate a high content of organic matter in the soil leading to C_{THP} much higher than for soils with low organic matter content.

References

1. Accardi, D., Gschwend, P.M. – Assessing the combined of roles of natural organic matter and black carbon as sorbents in heterogeneous organic matter on phenanthrene sorption: Different sediments, *Environ. Sci. Technol.*, **36**, 2002, pp. 21–29.
2. Balnois, E., Wilkinson, K.J., Lead, R., Buffle, J. – Atomic Force Microscopy of Humic Substances: Effects of pH and Ionic Strength, *Environmental Science & Technology*, **33**, Issue 21, November 1, 1999, pp. 3911-3917.
3. Bohaček, Z., Bezděc, K., Kovarova, M., Hanak, J., Tpoul, J., Muller, P. – Characteristics of organic matter and contents of some ubiquitous hydrophobic organic pollutants in selected soils and sediments, *Bulletin of Geosciences*, **78**, 3, 2003, pp. 179-204.
4. Dumitran, C., Onutu, I. – Environmental Risk analysis for crude oil soil pollution, *Carpathian Journal of Earth and Environmental Sciences*, April 2010, Vol. 5, No. 1, pp. 83 – 92.
5. Dumitran, C. – *Contribuţii la studiul extracţiei compuşilor organici hidrofobi din solurile contaminate cu ţiţei şi la evaluarea riscului de mediu*, Teza de doctorat, UPG Ploiesti, 2010, p. 167-178.
6. Ekholm, P., Blomberg E., Claesson, P., Auflem, I.H., Sjoblom, J., Kornfeldt, A. – A Quartz Crystal Microbalance Study of the Adsorption of Asphaltenes and Resins Onto a Hydrophilic Surface, *J. Colloid Interface Sci*., **247**, 2002, pp. 342-350.
7. Gauthier, T.H., Seitz, W., Grant, C. – Effect of structural and compositional variations of dissolved humic materials on pyrene KOC values, *Environ. Sci. Technol.*, **21**, 1987, pp. 243–248.
8. Juergen, P., Frank, K. – Sorption of Very Hydrophobic Organic Compounds (VHOCs) on Dissolved Humic Organic Matter (DOM), *Environ. Sci. Technol.*, **32**, 2001, pp. 45-48.
9. Jaweon, P., Gary., A. – Characterization of clean and natural organic matter (NOM) fouled NF and UF membranes, and foulants characterization, *Desalination*, **118**, 2004, pp. 101-108.
10. Kordei, W., Dassenakis, M. – The importance of natural organic material for environmental process in waters and soils, *Pure& Appl. Chem.*, **69**, 7, 2001, pp. 1571-1600.
11. Stevenson, F.J. – *Humus Chemistry*, Library of Congress Cataloging, USA, 1994, pp. 177-180.
12. Xia, G., Ball, P. – Polanyi-Based Models for the Competitive Sorption of Low-Polarity Organic Contaminants on a Natural Sorbent, *Environmental Science and Technology,* **34**, 7, 2000, pp. 1246 – 1253.
13. Zbynek, B., Josef, B. – Characteristic of organic matter and contents of some ubiquitous hydrophobic organic pollutants in selected soils and sediments, *Bulletin of Geosciences*, **78**, 3**,** 2003, pp. 179-204.

Contribuţii la remedierea şi reconstructia ecologică a solurilor poluate cu ţiţei şi produse petroliere

Rezumat

Articolul evidenţiază legatura dintre analizele pedologice executate pentru diferite profile de sol (pH, reactivitate sol, conţinut de humus, conţinut de fosfor şi potasiu, diagrama garnulometrică, permeabilitatea, carbon organic total, cloruri, fosfaţi, substanţe minerale, fier) şi caracteristicile fizico-chimice reprezentative poluantului petrolier (densitate, viscozitate, analiza SARA), care influenţează alegerea tehnologiilor de remediere a solurilor care urmează să fie redate circuitului agricol. Studiul experimental realizat a demonstrat cum materia organică din sol, pH-ul solului modificat datorită amendamentelor agricole, conţinutul de O_2 şi oxizii de fier din sol pot influenţa extracţia hidrocarburilor din solul poluat.