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SOIL CONTAMINATION WITH PETROLEUM COMPOUNDS AND HEAVY METALS - CASE STUDY

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Abstract

Crude oil, petroleum fuel and oil products represent most environmental contaminant of soil and the 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. The main target of this paper is the study of the critical soil pollutants in a Romanian refinery area where soil pollution with petroleum products is one of the main sources of soil contamination. The methodology of study is measuring and monitoring of the pollutants and codify soil pollution profile. The chemical analysis of the crude oil-contaminated site included different groups of contaminants: PAHs, BTEX compounds, and heavy metals determined in the soil samples from the investigated area. The analytical procedure to measure petroleum contaminants and the heavy metal concentrations was performed according to standard methods in force: SR ISO 13877:1999, ISO 22155:2011 SR ISO 11047:1999 and ISO 20280:2007, and with the appropriate equipment. The results are shown that there is a plenty of pollutants in the critical situation and higher than standard.

Key words*: soil contaminated, oil industry, total hydrocarbons, heavy metals, analytical methods.*

INTRODUCTION

Today is widely recognized that the contaminated lands represent a potential threat to human health, and it has led to international efforts to remedy many of these sites, either as a response to the risk of adverse health or environmental effects caused by contamination or to enable the site to be redeveloped for use (Marinescu et al., 2010; Onutu et al., 2010; Diphare, 2014).

In refinery, and vicinity of a refinery, the major sources of petroleum contamination are constituted of crude oil and petroleum products spills on soil, leakages from pipelines, underground and surface fuel storage tanks, indiscriminate spills and careless disposal and mismanagement of waste and other petroleum by-products (Onutu, 2010; Onutu et al., 2015; Popa et al., 2016).

Petroleum refining processes led to the generation of large quantities of oil sludge consisting of hydrophobic substances and substances resistant to biodegradation. Soil oil contamination is a result of fuel storage tank leakages, crude oil spill sand refinery waste disposal. Such sites often contain organic contaminants including benzene, toluene, ethylbenzene, and petroleum hydrocarbons (Pinedo et al., 2013). The solubility of mentioned compounds, in pure water is low, and they are strongly adsorbed in soils, especially onto terrestrial colloids (Wang et al., 2012; Mulligan et al., 2001).

Petroleum fuels and oils are complex mixtures of hydrocarbons and the compositions of these products are made up of several hundred hydrocarbon compounds that could determine the health risk. This is the reason that petroleum fuel or oil contaminated sites have been characterized by two measures; specific indicator compounds called the chemicals of concern (COCs) and by the total of all the petroleum hydrocarbons, called total petroleum hydrocarbons (TPH). The indicator COCs had human health risk derived closure levels, but TPH did not have closure levels based upon human health effects (RISC Technical Guide, 2006).

Heavy metals constitute an ill-defined group of inorganic chemical hazards, and those most commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) (Wuana et al., 2011).

Pollutants specific, to a former ramp and depot for loading and unloading petroleum products in a Romanian refinery, are total petroleum

hydrocarbon (TPH) benzene and mono and di-alkylated benzene compounds: toluene, ethylbenzenes and (ortho, para and meta) xylenes, lead compounds (Adeniyi et al., 2002).
In this context, the paper presents the assessment of soils exposed to oil products expressed by total petroleum hydrocarbons (TPH) measure.
However, the TPH assessment does not indicate the individual substances that may produce contamination. This study, focused on 36 samples collected from a certain site, evaluates TPH and BTEX concentrations in soils. Several indices of pollution are defined for the assessment of individual variables (TPH, B, T, E, and X) and lead content. This preliminary study provides useful information about the soil processes and current trends in quality assessment methodology (Hernandez et al., 2013).

MATERIALS AND METHODS

In order to obtain accurate measurements of specific pollutants a proper sample collection and preservation were applied.
TPH samples, especially unknown petroleum products and gasoline range organics samples were collected and preserved in a manner that minimizes the volatilization and biodegradation of the hydrocarbons. Soil samples were collected according to the methodology in place so that the sampling program provided (Onutu et al., 2012).
The values determined for Total Petroleum Hydrocarbons (TPH), Benzene, Toluene, Ethylbenzene, Xylenes (BTEX) and Lead in soil samples were compared with the values established by *Ministry of Waters*, *Forests and Environmental Protection* (MWFEP) - Order no. 756/1997 (Table 3).
In this experimental study, soil samples taken from the investigated area, has conducted a series of analyzes for determining the following:
- Total Petroleum Hydrocarbons (TPH) content;
- Benzene, Toluene, Ethylbenzene, Xylenes (BTEX) concentrations;
- Lead content.

Sampling 36 samples of soil were taken, over the length of the drilled range, in the absence of precipitation (Table 1).

Table 1. Coding of boreholes and recollected samples

Drilling Cod	Sampling point coding	Sample names
F1	F1/0.5 cm	soil from the depth of 0.50 cm
	F1/1 m	soil from the depth of 1 m
	F1/3 m	soil from the depth of 3 m
	F1/8 m	soil from the depth of 8 m
F2	F2/0.5 cm	soil from the depth of 0.50 cm
	F2/1 m	soil from the depth of 1 m
	F2/3 m	soil from the depth of 3 m
	F2/8 m	soil from the depth of 8 m
F3	F3/0.5 cm	soil from the depth of 0.50cm
	F3/1 m	soil from the depth of 1 m
	F3/3 m	soil from the depth of 3 m
	F3 /8 m	soil from the depth of 8 m
F4	F4/0.5 cm	soil from the depth of 0.50m
	F4/1 m	soil from the depth of 1 m
	F4/3 m	soil from the depth of 3 m
	F4/8 m	soil from the depth of 8 m
F5	F5/0.5 cm	soil from the depth of 0.50 cm
	F5/1 m	soil from the depth of 1 m
	F5/3 m	soil from the depth of 3 m
	F5/8 m	soil from the depth of 8 m
F6	F6/0.5 cm	soil from the depth of 0.50 cm
	F6/1 m	soil from the depth of 1 m
	F6/3 m	soil from the depth of 3 m
	F6/8 m	soil from the depth of 8 m
F7	F7/0.5 cm	soil from the depth of 0.50 cm
	F7/1 m	soil from the depth of 1 m
	F7/3 m	soil from the depth of 3 m
	F7/8 m	soil from the depth of 8 m
F8	F8/0.5 cm	soil from the depth of 0.50 cm
	F8/1 m	soil from the depth of 1 m
	F8/3 m	soil from the depth of 3 m
	F8/8 m	soil from the depth of 8 m
F9	F9/0.5 cm	soil from the depth of 0.50cm
	F9/1 m	soil from the depth of 1 m
	F9/3 m	soil from the depth of 3 m
	F9/8 m	soil from the depth of 8 m

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Sampling and transport of soil samples:
- collecting samples in glass containers with a lid;
- storage of samples under refrigeration conditions before and during transport to the laboratory in accordance with the storage procedures.

Analytical methods of analysis.

The analyses were carried out in the laboratories of the Faculty of Oil and Petrochemical Technology and EUROTOTAL Company. Because gas chromatography (GC) still remains the most important single technique for oil spill identification due to its equipment, relatively cheap and readily available, and easy to operate the determination of hydrocarbons in the soil was performed on the samples, using standard SR EN ISO 16 703 and GC-FID apparatus (Dumitran et al., 2009; 2010).

Apparatus and methods of analysis used to determine soil pollutants (TPH, PAH, B, T, E, X and lead content) for case study are presented in Table 2.

Table 2. Apparatus and methods of analysis used to determine soil pollutants

Current number	Polluant	Matrix	Standard Method	Used Equipment	Accredited/non-accredited method
1	Total Petroleum Hydrocarbons content C10-C40	Soil	SR EN ISO 16703:2011	GC –FID Dani Instrument Master Fast GC-AS	Accredited method
2	Determination of aromatic hydrocarbons: benzene, toluene, o, m, p-xilenes and ethylbenzene by gas chromatography	Soil	SR EN ISO 22155:2013	GC ECD Dani Instruments Master Fast GC-HS	Accredited method
3.	Determination of polycyclic aromatic hydrocarbons (HAPs) (naphthalene, phenanthrene, fluoranthene, pyrene, benzo (b) fluoranthene, benzo (k) fluoranthene, benz (a) pyrene, dibenzo (a,h) anthracene1, 2, 3 - cd) of pyrene	Soil	SR ISO 13877:1999	U HPLC Thermo Scientific Dionex Ultimate 3000	Non-Accredited method
4	Determination of lead content	soil	SR ISO 11047/1999	Atomic flame absorption spectrophotometer PG Instruments AA500	Accredited method

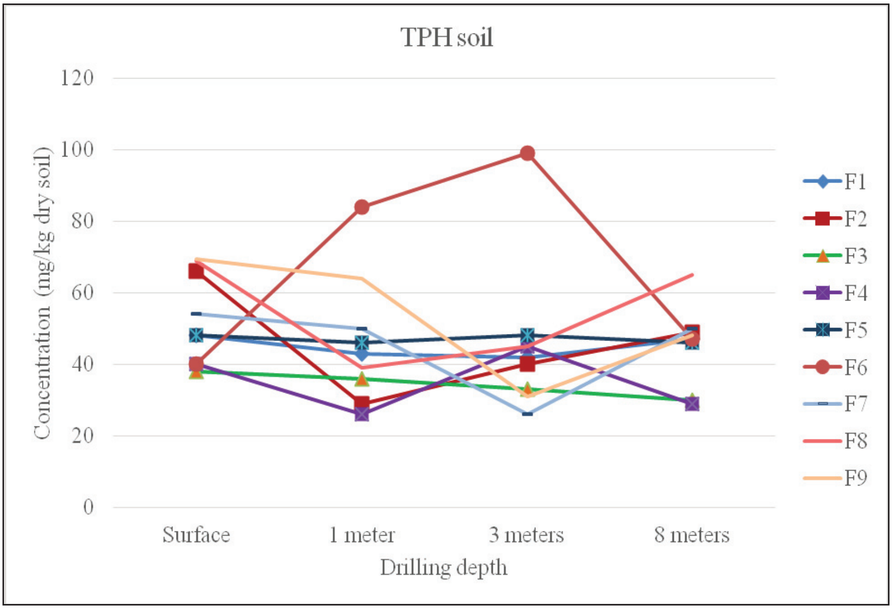

Figure 1. Total Hydrocarbons from Petrol (THP) in contaminated soil for the 36 samples and the 9 coded drillings

Figure 2. View of a broken crude oil pipeline

RESULTS AND DISCUSSIONS

Taking into account the results of the determinations carried out on the soil samples compared to the threshold values established by Ministerial Order 756/1997, the following aspects were highlighted: The measured values for Total Petroleum Hydrocarbons on soil samples are under and some around the normal values below the alert threshold, for less sensitive soil (industrial use) in each sampling bore at all soil sampling depths. The determined values are around the normal values as outlined in Figure 1. In addition to TPH, measurements of the individual benzene, toluene, ethylbenzene, and xylene (BTEX) compounds are routinely made for purposes of defining the nature and extent of fuel spills.

Benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds are always present in gasoline and should be tested for at all gasoline contaminated sites. For an improved assessment of the soil quality were included aromatic volatile hydrocarbons like benzene, toluene, ethylbenzene and xylenes (BTEX). (Table 4).

The measured values of the BTEX content for all analyzed samples are above the normal values, set by the legislation in force, but below the alert threshold (Table 4).

For several years (1973–1996) leaded gasoline was used as octanic additive. After 1996, lead compounds EDB (ethylene dibromide) and EDC (ethylene dichloride) are unlikely to be present at environmentally significant levels in most gasoline releases. However, leaded gasoline is still allowed for off-road uses such as aviation, farm equipment, marine engines and racing fuels.

In addition to the inorganic compounds of lead, there are a number of organo lead compounds such as tetraethyl lead.

The toxicities and environmental effects of organo lead compounds are particularly noteworthy because of the former widespread use and distribution of tetraethyl lead as a gasoline additive (Stoian et al.,2017).

For these reasons, the lead, EDB and EDC has to be tested to establish whether these contaminants are present at the site. If they are found, additional testing should be conducted to establish the extent of soil and groundwater contamination (Onutu et al., 2015).

Table 3. Threshould values according to Ministerial Order (M.O.) 756/1997.

Contaminant	Normal values, mg/kg d.s.	Alert thresholds, mg/kg d.s	Intervention thresholds, mg/kg d.s
TPHs	100	1000	2000
B	<0.01	0.5	2.0
EB	<0.05	10.0	50.0
T	<0.05	30.0	100.0
X	<0.05	15.0	25.0
Lead	<20	250	1000

Table 4. BTEX values according to Ministerial Order (M.O.) 756/1997

Contaminant	Normal values, mg/kg d.s.	Determined values, mg/kg d.s.	Alert thresholds, mg/kg d.s
B	<0.01	<0.22	0.5
EB	<0.05	<0.23	10.0
T	<0.05	<0.24	30.0
X (M+P)	<0.05	<0.47	15
X (O	0.05	<0.24	15
Lead	<20	48	250

Note. The the values obtained experimentally and presented in the table represent average values of the contaminants studied. These values were exceeded only in isolated cases.

Thus, the lead content measured on soil samples record values below the Alert Threshold (250 mg/kg d.s.) from the surface to the depth of about 3 m, except values from the depth (8 m) for drilling F1, F4, F8, F9 exceeding the alert threshold value (250 mg/kg dry soil) and the depth values (8 m) at drills F2, F3, F5, F6, F7 exceed the intervention threshold/kg su (Table 5).

The determined values are around normal values up to a depth of about 3 m in each soil sampling drill, and at 8 m depths exceeds the

alert value (250 mg/kg su) or the intervention value (1000 mg/kg su).
Interestingly, a higher lead content is found on soil that has less TPH content, which is explained by the fact that the site was contaminated with tetraethyl lead.

Table 5. Lead content values according to Ministerial Order (M.O.) 756/1997

Crt. no.	Sampling point coding	Determined values, mg/kg d.s.	Crt. no.	Sampling point coding	Determined values, mg/kg d.s.
1	F1/0.5cm	**47**	19	F5/3m	**197.5**
2	F1/1m	**47**	20	F5/8m	**1141**
3	F1/3m	**70**	21	F6/0.5 cm	**65**
4	F1/8m	**625**	22	F6/1m	**42**
5	F2/0.5cm	**57**	23	F6/3m	**59**
6	F2/1m	**58**	24	F6/8m	**1580**
7	F2/3m	**149**	25	F7/0.5 cm	**45**
8	F2/8m	**1255**	26	F7/1m	**41**
9	F3/0.5cm	**66**	27	F7/3m	**132**
10	F3/1m	**72**	28	F7/8m	**1705**
11	F3/3m	**91**	29	F8/0.5 cm	**25**
12	F3/8m	**1640**	30	F8/1m	**46**
13	F4/0.5cm	**37**	31	F8/3m	**120**
14	F4/1m	**37**	32	F8/8m	**644**
15	F4/3m	**48**	33	F9/0.5 cm	**40**
16	F4/8m	**554**	34	F9/1m	**37**
17	F5/0.5cm	**20**	35	F9/3m	**110**
18	F5/1m	**45.5**	36	F9/8m	

CONCLUSIONS

Historically, there are numerous sites at which petroleum spills or leaks have occurred. Crude oil and fuel storage tanks pump houses, and fuel lines can be typical sources of unexpected releases of fuels to the environment.
Among the phases that make up the Contaminated Site Management procedure, as stated in the National Strategy, namely: (1) inventory, (2) historical/preliminary investigation, (3) detailed investigation, (4) actions for correction, (5) evaluation of the contaminated sites management process, the finalization of the corrective actions, in this paper was described the stage 3 - the detailed investigation.
The experimental results on soil pollution related to a former petroleum storage facility (leaded tetraethyl lead, petroleum, diesel oil) showed that such activity does not affect soil for 20-30 years if the equipment used is properly maintained and its operation takes place according to technological requirements.
The assessment of soils exposed to crude oil or petroleum products can be conducted through the comparison between a measured concentration and an intervention value (IV). Several national policies include the IV based on the so called total petroleum hydrocarbons (TPH) measure. However, the TPH assessment does not indicate the individual substances that may produce contamination.
The soil quality assessment can be improved by including common hazardous compounds as polycyclic aromatic hydrocarbons (PAHs) and aromatic volatile hydrocarbons like benzene, toluene, ethylbenzene and xylenes (BTEX).
This study, based on 36 samples collected from investigated site, allows to that TPH and PAH concentrations above the IV are mainly found in medium and heavy oil products such as diesel and heavy oil. On the other hand, unacceptable BTEX concentrations are reached in soils contaminated with gasoline and kerosene. The TPH assessment suggests the need for further action to include lighter products. This work provides useful information about the soil quality assessment methodology of oil products in soils, focussing the analysis into the substances that mainly cause the risk.
Critical values for contaminant are retained as soil remediation standard. The methodology for site specific risk assessment is based on the approach followed to derive soil remediation standards. Finally, the ecological restoration and reconstruction of the soils affected by the pollution involves an assembly of technical works and works of agropedoameliorative character.
The agropedoameliorative work to be carried out is based on a pedological study, in one cycle or in a series of cycles, for each polluted area, depending on the type of soil, the degree of pollution (pollution intensity) and the type of pollutant or sewage).

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