

## **ANALYTICAL INVESTIGATION OF SOME ORGANIC COMPOUNDS FROM CONTAMINATED AREAS WITH PETROLEUM PRODUCTS**

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**Abstract.** The role of soil within an ecosystem is to be an interface between air, surface water and underground water and also a zone of transit or accumulation for majority of organic and inorganic pollutants. Soil oil pollution represents a great environmental threat as it may contaminate the neighbourhood soils and surface and underground water. Contamination may occur anywhere during crude oil extraction and treatment, oil product transportation, storing and utilisation. The Romanian Environmental Legislation, according to Order 756/97 sets the normal values for petroleum products in soil below 100 mg/kg d.m., between 200–1000 mg/kg d.m. for alert levels and between 500–2000 mg/kg d.m. for intervention levels. The objectives of these analytical investigations were to assess the magnitude of pollution with petroleum hydrocarbons within oil field and the vertical and horizontal extent of soil contamination. The samples were collected in different locations throughout the Romanian oil fields and were analysed for mineral oil, BTEX compounds (benzene, toluene, methylbenzene and xylene) and PAHs (polycyclic arenic hydrocarbons) (11 compounds). Important differences of the organic level of pollution were observed as function of the position and depth of the soil samples investigated. The obtained values varied within the following ranges: from 25 to 1718 mg/kg for mineral oil, from 0.01 to 4.31 mg/kg for BTEX and from 0.01 to 8.43 mg/kg for PAHs.

*Keywords:* soil, analytical investigation, petroleum products.

### **AIMS AND BACKGROUND**

High toxicity and carcinogenic potential of some organic compounds are imposing analyses and monitoring of these pollutants from various water and soil categories, even if are present in traces.

The role of soil within an ecosystem is to be an interface between air, surface water and underground water and also a zone of transit or accumulation for majority of organic and inorganic pollutants.

Petroleum products are representing the most frequently category of pollutants founded both in water and in soil, the main sources of pollution being accidental spillages and discharges from industrial plants (oil extraction and treatment, refineries, storing and utilisation, gas stations) and transport vehicles. These types

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of pollution are causing damages of agricultural soil, leisure areas, and beaches and are inducing bad taste and smell in water, putting in danger the life of aquatic or terrestrial organisms.

For analyses of some organic compounds from soil and water were used analytical techniques like IR spectrometry<sup>1</sup> or gas chromatography<sup>2,3</sup> for mineral oil (TPH), high performance liquid chromatography<sup>4,5</sup> or gas chromatography<sup>6</sup> for determination of polycyclic arenic hydrocarbons (PAH) and gas chromatographic methods<sup>7,8</sup> for benzene, toluene, ethylbenzene, xylene (BTEX).

The Romanian environmental legislation, according to Order 756/97, sets the normal values for petroleum products in soil below 100 mg/kg d.m., between 200–1000 mg/kg d.m. for alert levels and between 500–2000 mg/kg d.m. for intervention levels. For PAH Order 756 establishes the normal value in soil below 0.1 mg/kg d.m., the alert levels between 7.5–25 mg/kg d.m., and the intervention levels between 15–150 mg/kg d.m. Also, for BTEX the normal value range is between 0.01–0.05 mg/kg d.m., the alert limits are between 0.25–30 mg/kg d.m. and the intervention levels range is 0.5–100 mg/kg d.m.

The analytical investigations objective was to assess the magnitude of pollution with TPH, BTEX and PAH within the Moinesti oil fields and the vertical and horizontal extent of soil contamination.

## EXPERIMENTAL

The samples were collected in different locations throughout the Romanian oil fields and analysed for TPH, BTEX compounds and PAHs (11 compounds).

The selection of optimal analytical method for soil samples depended mainly on the chemical structure of organic compounds and their concentration level.

*Determination of TPH from soil.* For determination of TPH from soil it was used the IR spectrometric method. A primary processing was performed in case of granulation of the soil sample higher than 2 mm and pollutants were heterogeneously distributed. It consisted of removal of various objects (vegetation, glass, metals, etc.) followed by chemical drying. The operation of chemical drying was performed through contact of equal quantities of soil (15 g) and anhydrous sodium sulphate (15 g). The mixture was kept at cold temperature for 12–16 h and periodically mixed in order to avoid formation of agglomerates. Liquid–solid extraction was applied as separation method using carbon tetrachloride as extraction solvents for 20 g dried soil. Purification of the compounds was realised by adding 5 g of magnesium silicate (particle size 60–100 mesh) to each extract.

The analyses of TPH were performed on a FTIR Spectrum BX II spectrometer Perkin Elmer, using natrium chloride cell with 0.3 cm optical length. The absorbance of organic extract obtained after the soil treatment was measured in range of 3100–2800  $\text{cm}^{-1}$  for three wavelengths:  $\nu_1 = 2925 \text{ cm}^{-1}$  ( $\text{CH}_2$  absorption band),

$\nu_2 = 2958 \text{ cm}^{-1}$  ( $\text{CH}_3$  absorption band) and  $\nu_3 = 3030 \text{ cm}^{-1}$  (CH arenic absorption band).

*Determination of BTEX from soil.* In order to analyse BTEX from soil it was applied a gas chromatographic method with a flame ionisation detector (FID) using a gas chromatograph Agilent 6890N. The soil samples (without drying) were extracted first with methanol and then with hexane, by shaking on a mechanical stirrer. The organic extract was washed with distilled water in a separatory funnel and then it was filtered on anhydrous sodium sulphate. For BTEX separation was used a HP-5 capillary column ( $30 \text{ m} \times 0.32 \text{ mm}$  intern diameter  $\times 0.25 \mu\text{m}$  film thickness). Operating parameters were as follows: carrier gas flow  $1 \text{ ml/min}$ , air flow  $400 \text{ ml/min}$ , hydrogen flow  $35 \text{ ml/min}$ , split/splitless injection, injection volume  $1 \mu\text{l}$ . The carrier gas was helium (99.9999% purity). The temperature program that ensured an optimal separation was: injector  $250^\circ\text{C}$ , detector  $275^\circ\text{C}$ , and column  $50^\circ\text{C}$  (5 min);  $3^\circ\text{C/min}$  to  $100^\circ\text{C}$ , and  $20^\circ\text{C/min}$  to  $225^\circ\text{C}$  (5 min).

*Determination of PAH from soil.* For the determination of PAH it was applied high performance liquid chromatographic method in reverse phase with UV detection. Soil samples (without drying) were subjected to solid-liquid extraction using acetone and petroleum ether by shaking on a mechanical stirrer. The organic extract was washed with distilled water in a separatory funnel for acetone and polar compounds removal and then it was filtered on anhydrium sodium sulphate. The extracts were concentrated by evaporation at low pressure using a rotary evaporator till  $1 \text{ ml}$ . Purification is realised by passing of extract through an aluminium oxide column and elution with petroleum ether and enrichment of residue with acetonitrile.

From soil samples were analysed 11 PAH compounds (naphthalene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(b+k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene). The analyses were performed on an Agilent 1100 liquid chromatograph. These compounds were separated on an reverse phase Lichrospher PAH C18 column ( $25 \times 4.6 \text{ mm}$ ,  $5 \mu\text{m}$ ) at  $20^\circ\text{C}$  temperature with the following mobile phase program: isocratic acetonitrile-water 60:40 (v/v) in 3 min, gradient acetonitrile-water 100:0 (v/v) in 12 min, isocratic acetonitrile-water 100:0 (v/v) in 15 min, flow  $1 \text{ ml/min}$ , injection volume  $10 \mu\text{l}$  and were detected at wavelength of  $254 \text{ nm}$ .

## RESULTS AND DISCUSSION

In order to assess the soil pollution level with organic compounds like TPH, BTEX and PAH generated by mineral oil extraction, by storage of mineral oil and of petroleum residues, were collected soil samples from many depth from three

type of zones: extraction oil derrick zone, petroleum deposit zone and oil residue deposit zone.

From extraction oil derrick zone were collected soil samples from three representative points of area (A, B, C) , in each case from four depths (0.3, 1, 3 and 5 m). A point was situated at 3 m from the oil derrick, B was situated at 10 m from the oil derrick and C was situated at 20 m from the oil derrick. For these three points were determined the organic pollutants concentrations (TPH, BTEX, PAH) and the results are presented in Figs 1, 2 and 3.

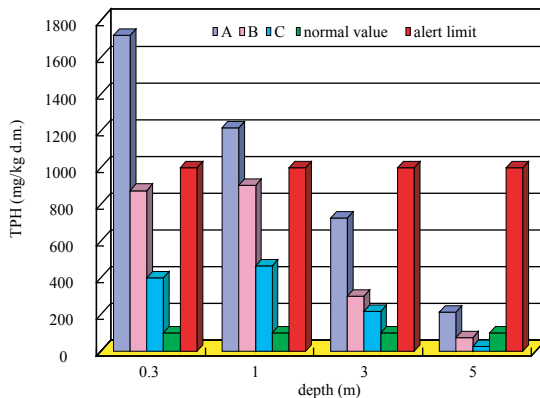


Fig. 1. Variation of TPH concentrations in the oil derrick zone

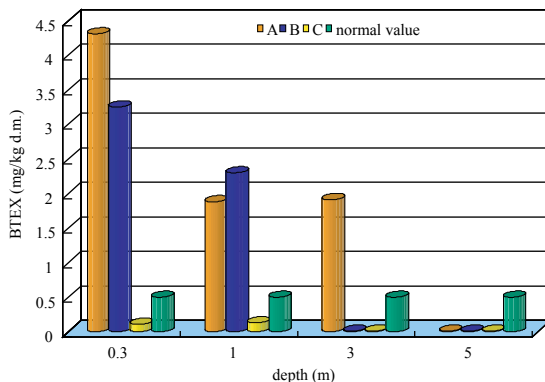
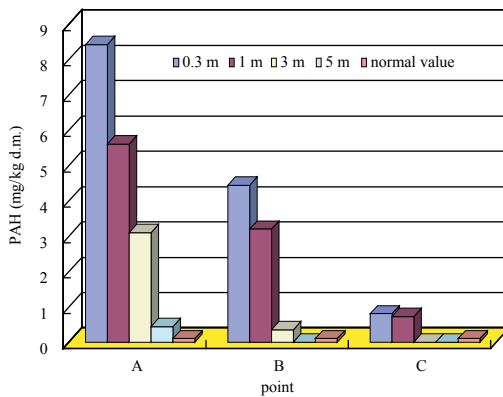
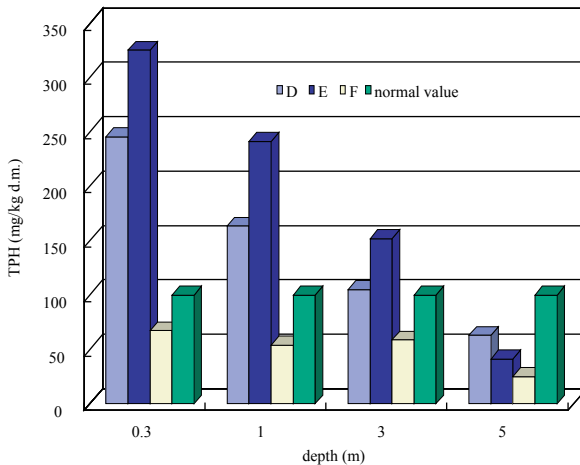


Fig. 2. Variation of BTEX concentrations in the oil derrick zone

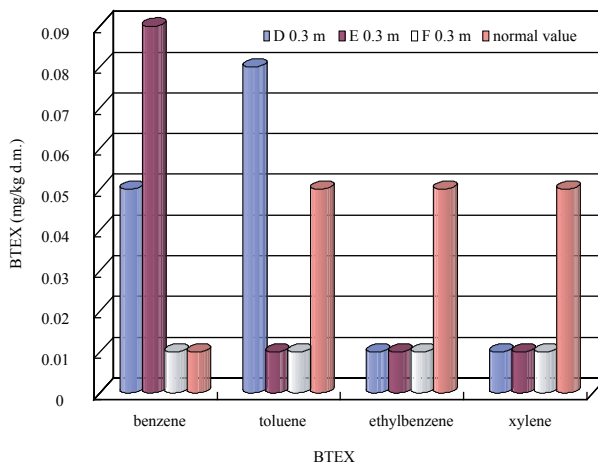


**Fig. 3.** Variation of PAH concentrations in the oil derrick zone

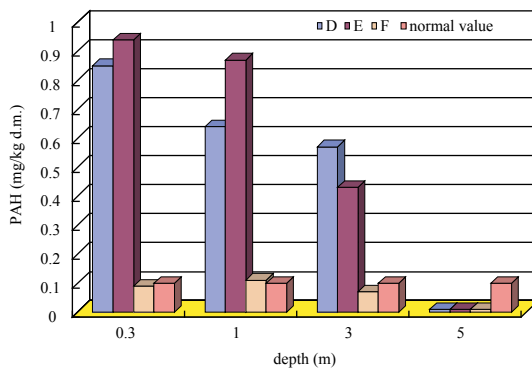
From oil deposit zone were collected samples from three different points: D and E points (situated near deposit) and F point (situated at border of deposit), from four depths (0.3 m, 1 m, 3 m and 5 m). Organic pollutants (TPH, BTEX, PAH) were analysed and the variation of concentration with depths is represented in Figs 4, 5 and 6.



**Fig. 4.** Variation of TPH concentrations in the mineral oil deposit zone

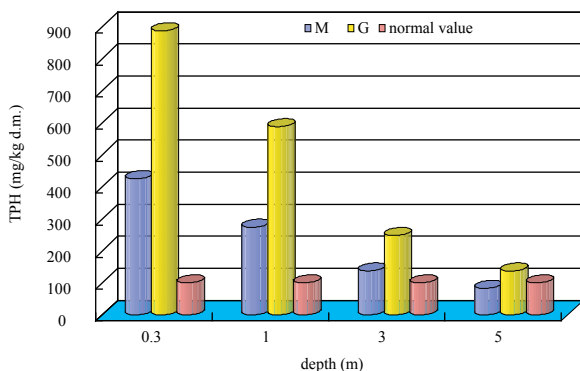


**Fig. 5.** Variation of BTEX concentrations at 0.3 m depth in the oil deposit zone

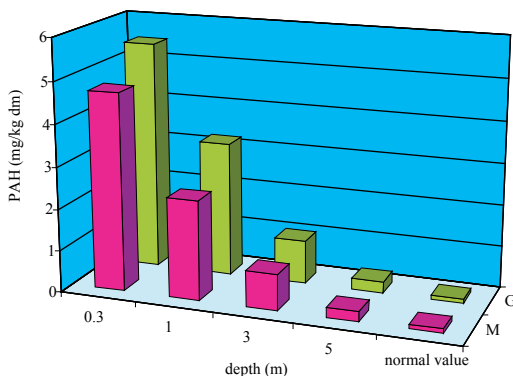


**Fig. 6.** Variation of PAH concentrations in the mineral oil deposit zone

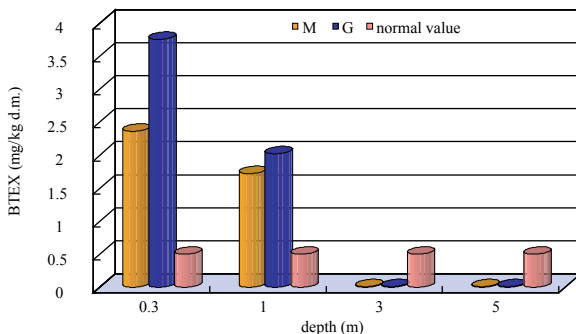
Also, for oil residue deposit zone used for storage of waste petroleum were collected soil samples from two different points (G – situated at 3 m from the waste oil deposit, and M – situated at 7 m from the waste oil deposit) from four depths (0.3, 1, 3 and 5 m). The concentrations of TPH, PAH and BTEX were quantified and presented in Figs 7, 8 and 9.



**Fig. 7.** Variation of TPH concentrations in the oil residue deposit zone



**Fig. 8.** Variation of PAH concentrations in the oil residue deposit zone



**Fig. 9.** Variation of BTEX concentrations in the oil residue deposit zone

From the results of analytical study obtained for the oil derrick zone it was observed that the pollution level increases horizontally with decrease of distance from the oil derrick, the most contaminated samples being from the point situated beside the oil derrick (A).

The two samples from surface soil ( $A_{0.3\text{ m}}$ ,  $A_{1\text{ m}}$ ) presented big TPH concentrations ( $A_{0.3\text{ m}}$  1718.5 mg/kg d.m.) which were situated in the intervention limit (in conformity with Order 756/1997); PAH concentrations are situated in the alert limit for majority of samples with exception of two samples ( $C_{3\text{ m}}$ ,  $C_{5\text{ m}}$ , situated at the biggest distance from the oil derrick) for which the concentrations are below the admissible value ( $<0.01$  mg/kg d.m.).

The BTEX concentrations are between 0.11–4.31 mg/kg d.m. being situated in the alert limit. The maximum concentration was recorded near the oil derrick ( $A_{0.3\text{ m}}$  4.31 mg/kg d.m. BTEX).

In the case of mineral oil deposit it was observed that the contamination is similar for the two points located beside of deposit (the D and E points). The TPH, BTEX and PAH concentrations are decreasing with depth. The concentrations of the three organic classes pollutants are situated in alert limit with exception of F point (located at border of deposit) which presented normal values for TPH ( $<100$  mg/kg d.m.) and for PAH ( $<0.1$  mg/kg d.m.). The BTEX concentrations were below the detection limit of method (0.01 mg/kg d.m.).

In case of the oil residue deposit it was observed a real contamination with mineral oil and the TPH, BTEX, PAH concentrations were in the alert limit. The pollution level for both points decreases with the depth of soil and with the distance from waste oil deposit. The maximum organic concentrations were recorded for surface soils samples:  $G_{0.3\text{ m}}$  (TPH 886.2 mg/kg d.m., BTEX 3.75 mg/kg d.m., PAH 4.72 mg/kg d.m.). The samples from big depth ( $G_{5\text{ m}}$ ,  $M_{5\text{ m}}$ ) had low concentrations for TPH and PAH and the BTEX values were situated below the detection limit of the method (0.01 mg/kg d.m.).

## CONCLUSIONS

From the results of the analytical study obtained for the oil derrick zone it was observed that the pollution level with TPH, PAH and BETX increase horizontally with decrease of distance from the oil derrick and vertical decrease with depth. The TPH concentrations were situated in the intervention limit only for  $A_{0.3\text{ m}}$  (1718 mg/kg d.m.) and  $A_{1\text{ m}}$  (1215 mg/kg d.m.) point which were near the pollution source. The other soil samples from this zone had TPH values situated in the alert limit.

In the oil derrick zone the PAH concentrations were situated in the alert limit for the majority of the soil samples with exception of two samples ( $C_{3\text{ m}}$ ,  $C_{5\text{ m}}$ , situated at the biggest distance from the oil derrick). The BTEX concentrations were between 0.11–4.31 mg/kg d.m. being situated in the alert limit. The maximum concentration was recorded near the oil derrick at surface ( $A_{0.3\text{ m}}$  4.31 mg/kg d.m. BTEX).

In the case of mineral oil deposit it was observed that the contamination is similar for the two points located near of deposit (the D and E points). The TPH,



BTEX and PAH concentrations decrease with depth and with the increasing the distance from contamination source. The TPH and PAH values were situated in the alert limit only for the points situated near of deposit (D and E) at the 0.3–3 m depth. The BTEX concentrations had low values ( $D_{0.3\text{ m}}$ : 0.13 mg/kg d.m.,  $E_{0.3\text{ m}}$ : 0.09 mg/kg d.m.) being situated in the alert limit only for surface soil of the deposit.

In the oil residue deposit it was observed a real contamination with mineral oil and the TPH, BTEX, PAH concentrations were in the alert limit. The pollution level for both points decreases with the depth of soil and with the distance from waste oil deposit. The maximum organic concentrations were recorded for surface soils samples:  $G_{0.3\text{ m}}$  (TPH 886.2 mg/kg d.m., BTEX 3.75 mg/kg d.m., PAH 4.72 mg/kg d.m.).

Using the results of this analytical study the authorities and oil companies can take measures for remediation of the areas contaminated with petroleum products.

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