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USE OF BIODEGRADABLE SORBENTS TO THE DECONTAMINATION OF POLLUTED SOILS

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ABSTRACT

The paper presents the decontamination of soils polluted with diesel, oils and other petroleum products. Soil decontamination is applied in-situ and ex-situ, depending on the surface and depth of the polluted area. The treatment time was 152 days, after which total hydrocarbon oil concentrations decreased for all experimental samples. The highest efficiency in reducing the concentration of petroleum products was in the case of samples treated with biodegradable sorbent and in the case of those treated with biodegradable sorbent mixture and biological sludge. Biodegradable non-waste materials have been used. The risk of migration of deep pollutants is low in the ex-situ version. Decontamination time is longer for high yields. In the case of older pollution, decontamination yields are low due to the presence of some 35% compounds, which do not migrate and are difficult to biodegrade under normal conditions.

KEYWORDS: decontamination, biodegradable sorbent, polluted soils

1. Introduction

Based on data provided by the national soil quality monitoring system, it is estimated that 900,000 ha of soil are chemically polluted, of which 200,000 ha are excessively polluted, making them completely unproductive. On an area of 50,000 ha the soils in Romania are polluted with petroleum products; although the affected area has decreased in recent years, pollution continues to have a significant impact on the soil. Approx. 3,000 ha are completely removed from plant production, especially around oil exploration wells and along oil pipelines (in the counties of Prahova, Teleorman, Braila, Galati, Arges, Dambovita). The extraction of salt through the wells caused intense soil pollution on tens of hectares, with brine and oil products. Pollution of heavy metals and sulfur dioxide is identified especially in Baia Mare, Zlatna, Copsa Mica. To this was added the pollution with domestic and industrial residues. Soil irrigation in some rivers (Olt, Argeș, Mureș, Prahova, Siret), where toxic substances and oil products are discharged, leads to the progressive accumulation of pollutants in the soil, with serious consequences for human health.

The particular aspect of soil and groundwater pollution with crude oil and petroleum products for Romania is that it is a phenomenon with a history of more than 100 years, which started with the beginning of the exploitation of the oil deposits in the Prahova valley area and with the emergence and development petroleum industry.

In the field of ecological reconstruction of soils, measures were taken consisting of:

• inventorying contaminated, degraded land and other deficiencies;

• substantiating recommendations for good agricultural practices aimed at preserving and improving the quality of agricultural soils in line with international practices;

• substantiating ecological reconstruction measures for soils polluted with heavy metals;

• the scientific foundation of re-cultivation of mining waste dumps;

• leading experiments on the detoxification of soils polluted with crude oil, products and petroleum residues through bioremediation;

• performing technical and scientific substantiation of the polluting of polluted soils with mineral oils and polychlorinated biphenyls (PCBs) from Transelectrica S.A. [1].

Decontamination by sorbents is done by spreading them on the polluted surface, ensuring optimal contact between pollutant and sorbent. In some cases, bioremediation accelerators (strains of bacteria and/or fungi) are used, as well as the application of soil improvement treatments by

providing the aerobic conditions, ensuring the necessary humidity and restoring nutrient balance by fertilization.

Contaminated soil portions are in the vicinity of fuel depots, oil discharge areas, wagon repair areas, and railroad tracks. In accordance with the MAPPM Order no. 756/1997 for the approval of the Regulation on the assessment of environmental pollution, the reference values for traces of chemical elements in soils for oil hydrocarbons are presented in Table 1 [2, 3].

Table 1. *The reference values for traces of chemical elements in soils from petroleum hydrocarbon (mg/kg dry matter)*

Traces of pollutant	Normal values	Alert Thresholds / Types of Usage		Intervention Thresholds / Types of Usage	
		Sensitive	Less sensitive	Sensitive	Less sensitive
TPH (Total Petroleum Hydrocarbon)	< 100	200	1000	500	2000

2. Experiments and discussions

Biodegradable non-waste materials are used. Contaminated soil samples were taken which were treated with: a) NatureSorb type biodegradable sorbent; b) biodegradable mixture; c) biological sludge, respectively beech sawdust. The monitoring of the biodegradation process was carried out by periodic analyses of the quality indicators.

Sampling of soil samples was carried out in accordance with STAS 7184 / 1-1984 and Order no. 184/1997 of MAPPM. The soil samples were taken at two depths of 5 cm and 30 cm respectively [2, 4].

The number of samples taken was after the contaminated areas, 14 soil samples and two control samples.

For the collected soil samples the quality indicators were determined: pH, Humidity, Humus, Total Organic Carbon (TOC), Total Kjeldhal Nitrogen (NTK), Total Phosphorus and Total Petroleum Hydrocarbon (TPH) with the methods of analysis provided by the actual standards.

Following the laboratory analyses for soil samples, the values of the quality indicators presented in Table 2 were obtained.

Table 2. *Quality indicators of selected samples before treatment*

Nr. crt.	Sample code	Depth of sampling, [cm]	pH	TPH, [mg/kg d.m.]	TOC, [% d.m.]	NTK, [% d.m.]	P total, [mg/kg d.m.]
1.	Pm1	5	7.08	1859.12	1.25	0.142	0.073
2.	Pm2	30	7.14	1738.23	1.18	0.154	0.081
3.	Pm3	5	6.85	2147.34	1.82	0.098	0.085
4.	Pm4	30	6.94	1973.11	1.67	0.109	0.074

Each soil sample had 0.5 kg. Sample labelling was the following: 1) witness samples: Pm1, Pm2, Pm3, Pm4; 2) samples treated with NatureSorb biodegradable sorbent: Ps1, Ps2, Ps3, Ps4; 3) samples treated with sorbent mixture and biological sludge: Pss1, Pss2, Pss3, Pss4; 4) sorbent-treated samples of beech sawdust natural type cu: Psb1, Psb2, Psb3, Psb4.

The biodegradable sorbent was added in the ratio: concentration petroleum products / sorbent was 1: 3. To the samples labelled with „ss" was added 900 mL / biological sludge sample. The biological sludge used was taken from the recirculation system of a water treatment plant. In samples labelled with "sb", sawdust was added in the ratio: concentration petroleum / sawdust was 1:5. Ambient temperature was maintained between 21-35 °C to ensure optimal microorganism development and fluidity of petroleum products, and soil moisture was between 20-40% to favour absorption processes. No additional amounts of nutrients (nitrogen, phosphorus, etc.) were added, and sample aeration was done 3-4 days [5, 6].

The values for total petroleum hydrocarbons obtained are shown in Figures 1-3.

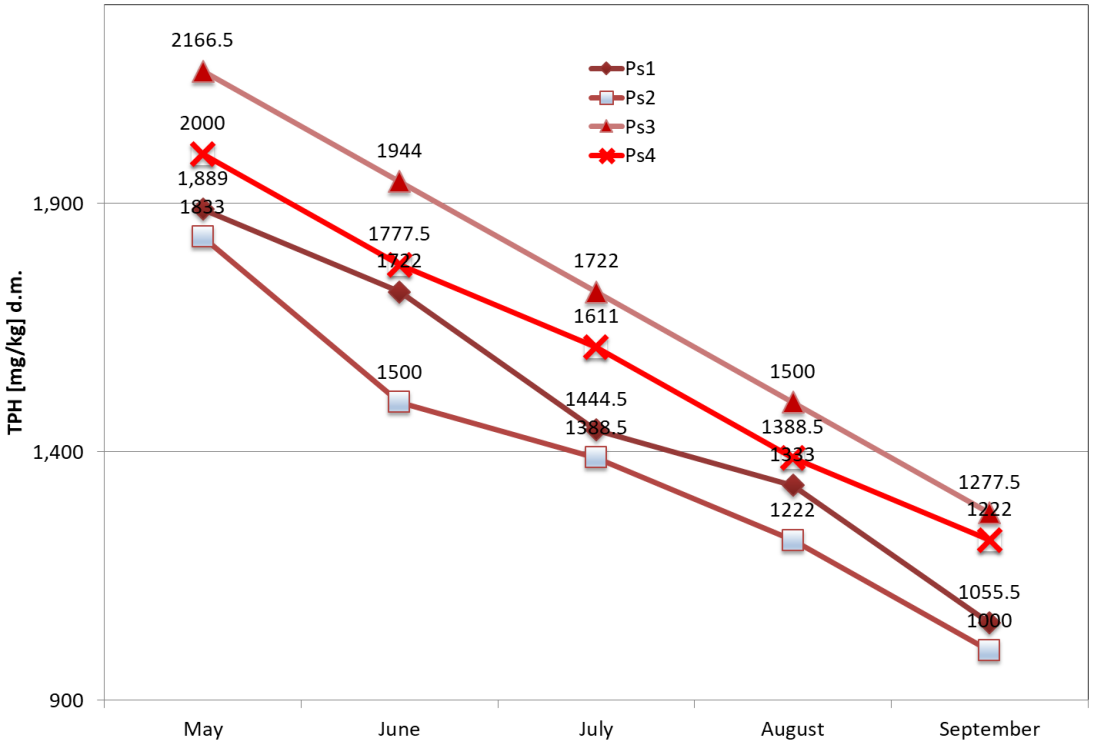

Fig. 1. *Variation of total petroleum hydrocarbon for samples treated with biodegradable sorbent*

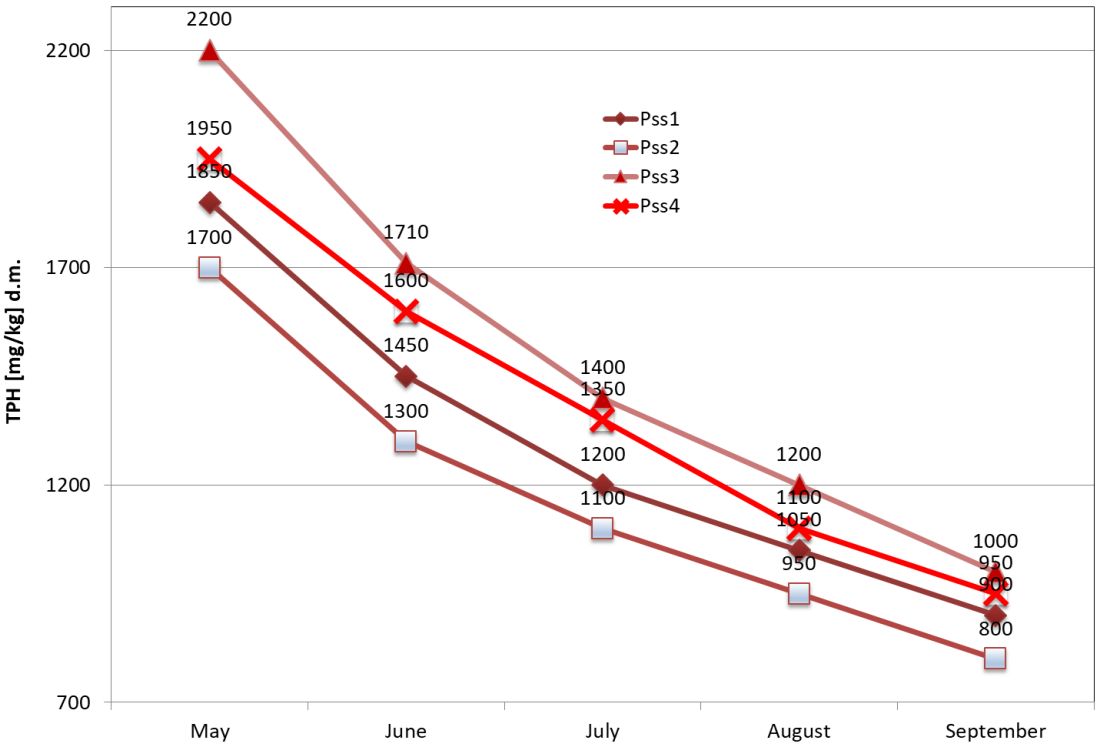

Fig. 2. *Variation of total petroleum hydrocarbon for samples treated with sorbent mixture and biological sludge*

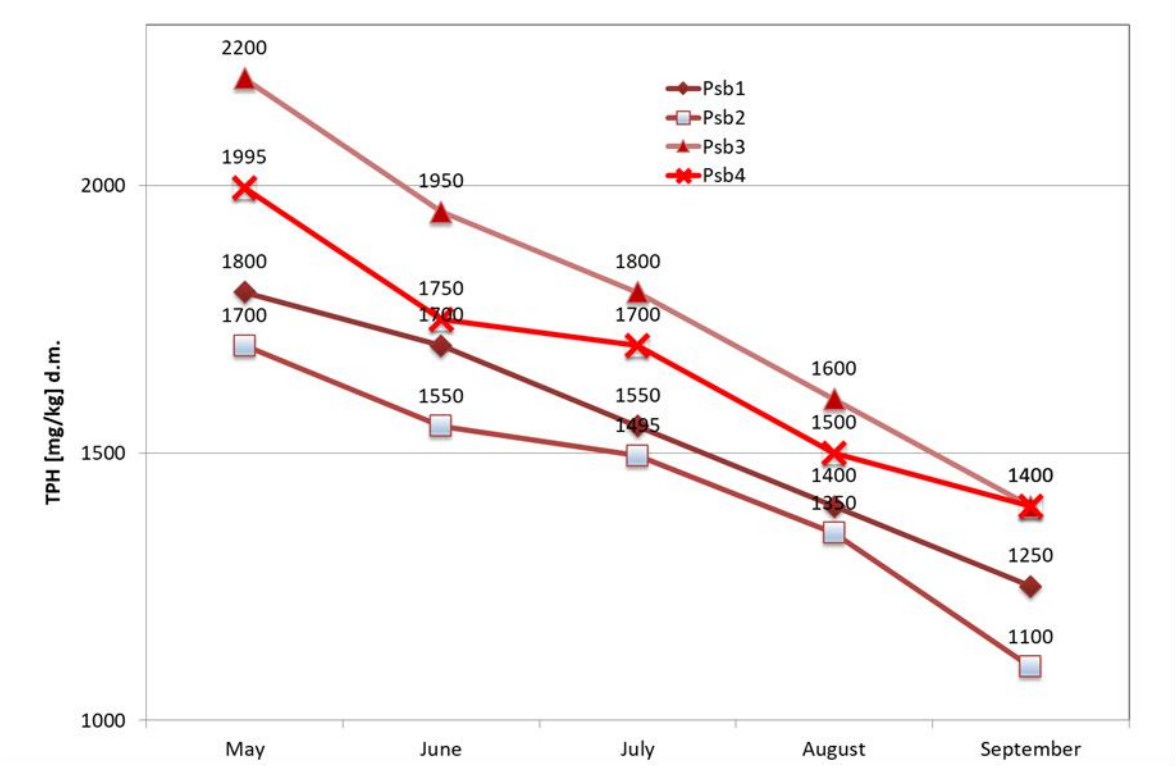

Fig. 3. *Variation of total petroleum hydrocarbon for samples treated with beech sawdust*

Following the analysis of the results obtained were ascertained the following:

a) the TPH values in the analysed samples exceeded the alert threshold of 1000 mg/kg d.m. for samples with code P1, P2, P4 as well as the intervention threshold of 2000 mg/kg d.m. for sample P3;

b) the gas chromatography mass spectrometry (GC/MS) analysis demonstrated that significant concentrations of diesel (C8-C22) and mineral oils (C20-C40), is relatively stable fractions, which migrate less in the soil, both horizontally and vertically;

c) pH values are within normal, neutral to slightly alkaline ranges, between 6.5 and 8.5;

d) the percentage of humus in the analysed samples indicates a low and medium supply, and the amount of nitrogen and phosphorus present in the samples is very low, indicating a very low nutritional intake [7, 8].

For samples with high initial concentrations of total oil in oil, P3 and P4, concentrations below the alert threshold required by the legislation were recorded only when treated with a mixture of sorbent and biological sludge.

Values of decontamination yields obtained for P3 and P4 samples are shown in Figures 4-5.

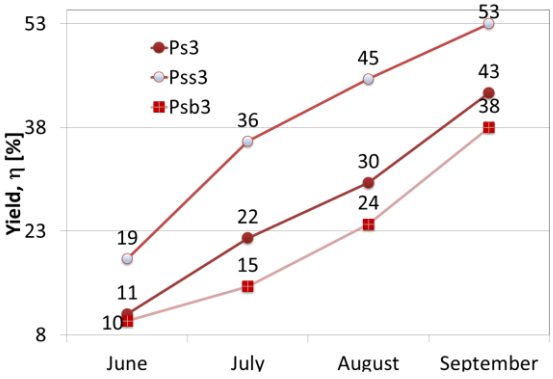

Fig. 4. *Decontamination yields for P3 samples*

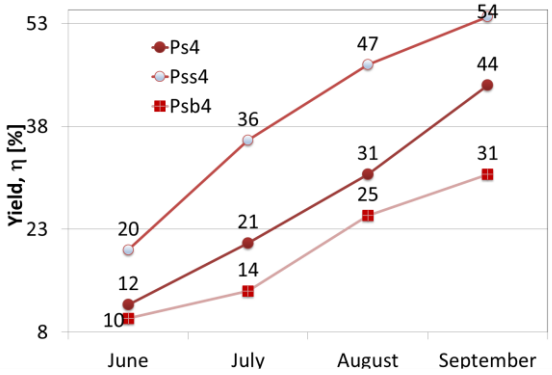

Fig. 5. *Decontamination yields for P4 samples*

3. Conclusions

After 153 days of treatment, total hydrocarbon oil concentrations showed a decrease for all experimental samples.

For sample Ps2 with large initial concentrations of total hydrocarbon oil, decreases in concentrations below the alert threshold required by the legislation were only observed when treated with biodegradable sorbent.

The highest efficiency of reducing the concentration of petroleum products was recorded for samples treated with biodegradable sorbent mixture and biological sludge Pss1, Pss2, Pss3, Pss4.

The decontamination yields showed a steady increase during the experiments, with the best yields being obtained for the samples added to the biodegradable sorbent and biological sludge with a maximum of 54%.

Satisfactory decontamination yields are also obtained for samples treated with biodegradable sorbent only, with values ranging from 43-44%.

The pollutant migration risk is low in the ex-situ version.

Decontamination time is long to get good returns.

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