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DETERMINATION OF PETROLEUM HYDROCARBONS CONTENT IN SOILS FROM SUPLACU DE BARCĂU, ROMANIA

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ABSTRACT. The level of pollution with petroleum compounds was evaluated in Suplacu de Barcău area based on the assessment of total petroleum hydrocarbons (TPH) concentrations in soil. As source of contamination, one active and another inactive petroleum extraction wells were chosen, and the concentrations were determined by fluorescence spectrometry. The results indicated alarming exceedances of the intervention thresholds, especially in the area where the activity is stopped, thus indicating long-term accumulation of pollutant and persistence in soil.

Key words: *petroleum hydrocarbons, soil pollution, TPH, fluorescence spectrometry*

INTRODUCTION

Soils polluted with petroleum hydrocarbons (PHCs) represent a serious concern for the environment due to various and multiple sources of contamination, such as extraction, refining, storage, transport, and petroleum marketing (Kaimi et al., 2007; Micle et al., 2018). PHCs represent a complex mixture of linear or branched alkanes, cycloalkanes, aromatic compounds, and other complex chemical compounds (e.g., asphaltenes), reason for which pollution with PHCs generates important imbalances in soil quality,

fertility, and biodiversity, therefore affecting the physico-chemical and biological components of the terrestrial ecosystems (Zhou et al., 2011). The main cause of pollution is represented by leaking and spilling of PHCs on the surface or in the underground soil, followed by long-term accumulation that, at the end of anthropogenic activity, exceeds the environmental regulations.

PHCs are characterized by a relatively high hydrophobicity, reason for which these pollutants have an increased ability to accumulate in soil compared to aquatic environments, where they bind to soil particles (Shirdam et al., 2008). In addition to low water solubility, PHCs feature high recalcitrant properties which lead to their persistence in soil (Khatibi and Hosseini, 2018). Therefore, the removal of PHC to perform soil decontamination might be difficult and expensive. Conventional soil remediation involves physical or chemical techniques (e.g., soil washing, solidification, stabilization, gaseous extraction, etc.) that have proven their efficiency, but involve high costs and high energy consumption (Kaimi et al., 2007; Jing et al., 2008). Another disadvantage of these conventional techniques is represented by the degradation of soil natural functions such as fertility, texture, and structure (Megharaj et al., 2011). Thus, phytoremediation is considered an alternative because the use of higher plants implies the use of energy from sunlight, maintains, and in some situations even improves, the natural functions of the soil, enhances the landscape of the contaminated area during the remediation process, and was indicated as a cost-effective technique (Banks et al., 2003; Glick, 2003; Shirdam et al., 2008).

Even though petroleum is not a renewable resource, it remains the main energy source in the world (Bastida et al., 2016), a reason for which soil contamination continues to spread, either at the surface, either in depth, thus becoming a critical environmental issue. This situation is present also in Romania, where petroleum is being exploited in different parts of the country. Suplacu de Barcău is one petroleum exploitation area, where active and inactive wells represent the source of contamination. Until today, a number of 2626 wells were drilled in the exploitation area (Ionescu et al., 2019). Geological data indicates that Suplacu de Barcău is the largest oil field in the Romanian sector of Pannonian Basin, with approximately 144 million barrels of recoverable oil (Dolton, 2006). The oil exploitation in Suplacu de Barcău area has started in 1961 with dissolved gas drive mechanism applied to monocline geological structure, starting from the uppermost part of reservoir (Asghari, 2009). Due to the very low recovery value, enhanced

oil recovery methods were applied since 1964. To increase the production rate, a thermal method (*in situ* combustion) was considered appropriate to extract the high viscosity oil from Suplacu de Bracău heavy oil reservoir (Carcoana, 1990). The oil extraction operations carried out over 60 years have led to a significant environmental impact. The main cause of soil pollution around the exploitation wells is represented by the oil spilling due to the improper maintenance, especially at the old wells, currently closed and decommissioned.

The aim of this investigation is to contribute to the environmental evaluation of the Suplacu de Barcău area considering contamination with PHCs. Soil samples were collected from the proximity of active and inactive wells used for petroleum extraction. Total petroleum hydrocarbons (TPHs) concentrations were determined to appreciate the level of pollution and how the soil quality was affected by their presence.

MATERIALS AND METHODS

Suplacu de Barcău is located in the north-western part of Romania, in Bihor (BH) County (figure 1). The study area was chosen in the petroleum exploitation area, found in the western part of the Suplacu de Barcău village. Agricultural fields are present in the proximity of the study area.

The environmental evaluation was based on 4 soil samples collected nearby the exploitation wells (figure. 1), from a depth between 10 and 15 cm, after the surface vegetation was removed. To compare the possible sources of contamination, two soil samples (P1 and P2) were taken nearby two active exploitation wells, and other two samples (P3 and P4) were taken from the proximity of two inactive exploitation wells. As reference, another soil sample (R) was collected from the shore of the accumulation lake from the area, located in the southern part of the village and considered to be unpolluted. Approximately 500 g of soil were collected from each sampling point with the use of a stainless steel hand auger, transferred to polyethylene bags, and transported at a constant temperature of 4 °C and in the absence of light.

The collected soil samples were dried at room temperature (approx. 20 °C, open air), homogenized, grounded and sieved to collect the fraction below 2 mm. A mass of 5 g of processed soil was transferred to glass tube, followed by the addition of 2 g of anhydrous sodium sulphate and 20 ml of

n-hexane. The mixture was vigorously shaken for 5 minutes, then the solvent was allowed to separate for 5 minutes and the vials were depressurized.

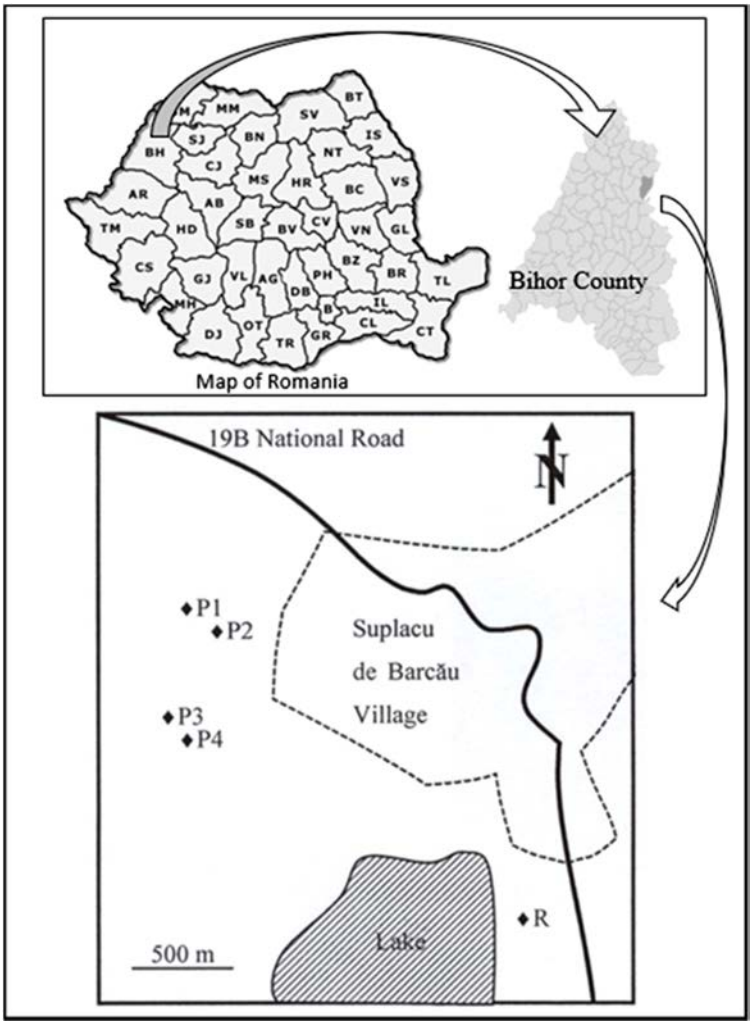

Fig. 1. *Localization of Suplacu de Barcău and field sampling points in the study area*

The organic fraction was separately collected and filtered through 0.20 µm pore size membrane filters before analysis (Brost et al., 2011), (www.oilinwatermonitors.com).

The TPHs concentration from the extracts was determined by fluorescence spectrometry using a Turner TD-500 fluorometer.

RESULTS AND DISCUSSION

The TPHs concentrations are presented in figure 2. The results indicated a high pollution with PHCs in the study area considering the environmental limits set for both sensitive and less sensitive uses of the soil.

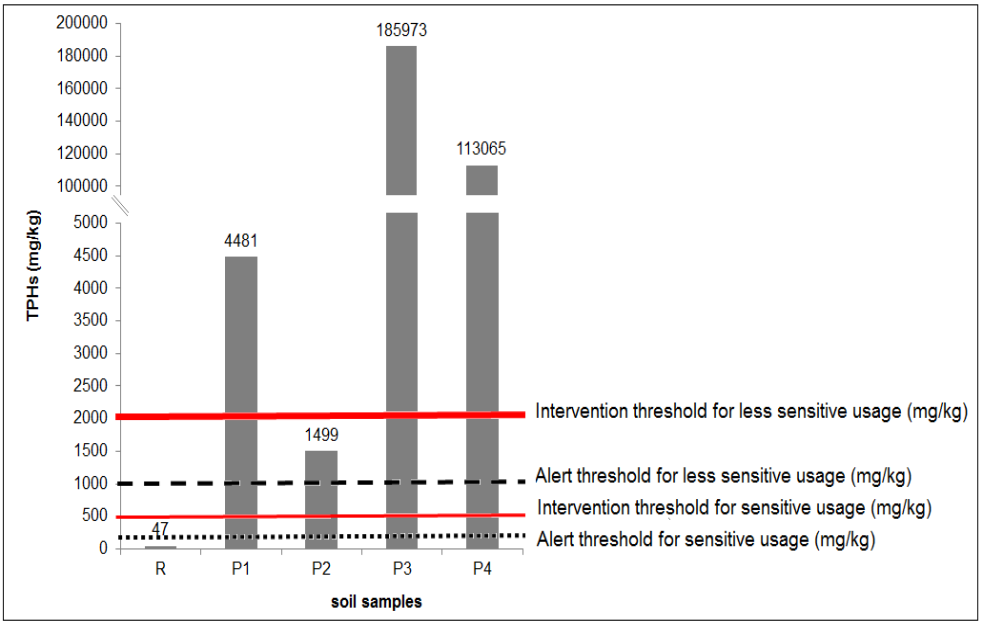

Fig. 2. *TPHs concentration in soil samples from the study and reference area, and the legislative threshold (Order 756/1997)*

Samples P1 and P2 were collected nearby two active wells. To assess the possible influence of PHCs in soil, the two sampling points were chosen considering the presence or absence of vegetation close to the extraction wells. P1 was characterized by a lack of vegetation within a radius of 1-2 meters from the extraction well, while P2 featured dried vegetation.

Correlating with the TPHs concentration (figure 2), where P1 is 3 times higher than P2, it can be assumed that the increased level of pollution is severely affecting the vegetation in the proximity of the well. While P1 was collected near the extraction well and directly under the petroleum transport pipe, P2 was established at a distance of 5 meters from the well. Based on the TPHs results, it can be assumed that the level of pollution at the surface of the soil decreases with the increase of distance from the source, but still exceeds the intervention threshold for sensitive usage (500 mg/kg), and exceeds the alert threshold for less sensitive usage (1000 mg/kg). For both situations, the environmental impact is significant and remediation processes should be implemented in the area.

To compare the sources of pollution, samples P3 and P4 were collected from the proximity of two inactive wells. Even though vegetation was present and appeared more abundant compared to the areas with active wells, most parts of it presented features of dried vegetation. It is important to highlight that the level of TPHs is 90 times higher than the intervention threshold for less sensitive soils (2000 mg/kg) in sample P3 and 56 times higher in sample P4, a reason for which remediation strategies are urgently demanded in the area. This high pollution might be a consequence of continuous and long-term contamination with PHCs caused by uncontrolled spills of petroleum. In some areas, the soil presented black spots at the surface, a feature that might be considered as evidence for the assumed spills. Even though the soil is covered by a layer of vegetation that might indicate the ability of native flora to develop, it is important to specify that only spontaneous vegetation, represented mainly by grass species, is present. Considering the long-term pollution, is known that resistant plants can develop adaptation strategies to specific pollutants, thus the present grass species might imply detoxification or tolerance mechanisms to PHCs.

Contamination problems with PHCs in the Suplacu de Barcău area have been indicated only in few studies, even though the assumptions upon environmental problems are well known at least at national level. Puia et al. (2016) assessed the level of TPHs in 4 sampling points within the oil exploitation area and revealed concentrations between 8850 – 46600 mg/kg. These concentrations also exceed the national thresholds (2000 mg/kg) and indicate different levels of contamination that can be influenced by typical sources of pollutant propagation found in a petroleum activity. These variations have been observed also by Costin et al. (2017) on soil samples

collected nearby other two exploitation wells (one active and another inactive). Close to the active well the TPHs concentration ranged between 347 – 5092 mg/kg, while in the proximity of the inactive well the TPH concentration increased, ranging between 24105 – 610801 mg/kg. Costin et al. (2017) identified exceedances of the legal thresholds also in the proximity of the air compression station located within the exploitation site, where TPHs concentrations ranged between 5135 – 12460 mg/kg.

Considering the observed variations of soil pollution, is assumed that the areas with inactive wells feature a higher pollution than the areas with an ongoing activity, as the case of active wells. Besides multiple factors that could be responsible for this variation, time and hydrophobicity of PHCs are the major ones. PHCs contamination has increase throughout the period of activity due to the availability of the source of pollution. During this time, PHCs will accumulate in soil because they cannot be dissolved by the atmospheric precipitations (Shirdam et al., 2008). Even though the source of propagation is stopped, the PHCs will remain present in soil due to recalcitrant properties which lead to their persistence in soil (Khatibi and Hosseini, 2018). Thus, the longer the period, the higher the contamination will be.

CONCLUSION

Contamination with TPHs has led to a high level of pollution in the Suplacu de Barcău exploitation area. Considering the alarming exceedances of the national thresholds for TPHs, the investigated area can be framed as contaminated site. Following the environmental protection regulations, the whole area should be subjected to remediation until the levels of pollution would decrease beneath the alert threshold. In order to apply a proper remediation technology, more studies should be performed to gain better knowledge on the spread of pollution at surface and in depth of the soil, and to characterize the reaction of PHCs with the soil matrix of the area.

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