**Justyna STANINSKA[1], Zuzanna SZCZEPANIAK[2], Paweł CYPLIK[1], Agnieszka PIOTROWSKA-CYPLIK[2]**
Poznań University of Life Sciences
[1] Department of Biotechnology and Food Microbiology
ul. Wojska Polskiego 48, 60-627 Poznań, Poland
[2] Institute of Food Technology of Plant Origin
ul. Wojska Polskiego 31, 60-624 Poznań, Poland

# THE EFFECT OF ORGANIC AND CLAY FRACTION ON POLYCYCLIC AROMATIC HYDROCARBONS MOBILITY IN SOIL MODEL SYSTEMS

*Summary*

*Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds, which accumulation in arable land is highly unfavorable phenomenon due to their toxic properties and adverse effects on yield as well as growth of plants. In order to determine the degree of PAHs exposure, the research on the sorption and accumulation of PAHs in various components of the soil is indispensable. The aim of this study was to define the effect of the organic and clay fraction on the mobility of PAHs. Experiments were carried out in column systems and the following solid phases (sorbents) were applied: a quartz sand (a control), a mixture of quartz sand and humic acids, a mixture of quartz sand and clay mineral - montmorillonite and systems combined with quartz sand, montmorillonite and humic acids. As a labile phase, the aqueous solution of phenanthrene (concentration of 0,5 mg·l$^{-1}$) was used. Quantification of PAHs in the eluate was carried out by a photoluminescence method. The obtained results indicate that the increase of both clay fraction and the humic acids resulted in an increase in the sorption of phenanthrene on a solid matrix. Moreover, the montmorillonite showed higher sorption than humic acids added in the form of a commercial preparation. Thus, it can be assumed that the soils characterized by favorable agronomic properties (a lot of clay fraction and organic matter) are particularly susceptible to the accumulation of organic compounds (e.g. PAHs). Additionally, this kind of soil – due to immobilization – is characterized by smaller capacity of natural bioremediation. These conclusions points to the need for monitoring of arable land, particularly areas with high emissions of PAHs to the environment.*
***Key words**: polycyclic aromatic hydrocarbons (PAHs), sorption, humic acids, clay fraction*

# WPŁYW FRAKCJI ORGANICZNEJ I ILASTEJ NA MOBILNOŚĆ WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W MODELOWYCH UKŁADACH GLEBOWYCH

*Streszczenie*

*Wielopierścieniowe węglowodory aromatyczne (WWA), z uwagi na toksyczne właściwości oraz niekorzystny wpływ na plonowanie i wzrost roślin stanowią grupę związków, których akumulacja w gruntach ornych jest zjawiskiem wysoce niepożądanym. W celu określenia stopnia narażenia niezbędna jest wiedza z zakresu badań podstawowych dotycząca sorpcji i akumulacji WWA w różnych komponentach glebowych. Celem badań było zdefiniowanie wpływu frakcji organicznej i ilastej na mobilność tych związków. Doświadczenie przeprowadzano w układach kolumnowych, natomiast fazę stałą (sorbent) stanowił odpowiednio: piasek kwarcowy (referencja), mieszanina piasku kwarcowego i kwasów humusowych, mieszanina piasku kwarcowego i minerału ilastego – montmorylonitu oraz układy kombinowane z piaskiem kwarcowym, montmorylonitem i kwasami humusowymi. Fazę labilną stanowił wodny roztwór fenantrenu o stężeniu 0,5 mg·l$^{-1}$. Oznaczeń ilościowych WWA w eluacie dokonano metodą fotoluminescencyjną. Badania dowiodły, iż wzrost zarówno udziału frakcji ilastej jak i ilości kwasów humusowych skutkował wzrostem sorpcji fenantrenu na matrycy stałej, przy czym montmorylonit wykazywał większe właściwości sorpcyjne niż kwasy humusowe dodawane w postaci komercyjnego preparatu. Można sądzić, iż gleby charakteryzujące się dobrymi właściwościami agronomicznymi (duży udział frakcji ilastej oraz materii organicznej) są szczególnie narażone na akumulację związków z grupy wielopierścieniowych węglowodorów aromatycznych a także w związku z immobilizacją - mniejszymi zdolnościami naturalnej bioremediacji. Wskazuje to na konieczność monitoringu tych gruntów ornych, szczególnie na obszarach gdzie występuje wysoka emisja WWA do środowiska.*
***Słowa kluczowe**: wielopierścieniowe węglowodory aromatyczne (WWA), sorpcja, kwasy humusowe, frakcja ilasta*

Abbreviations:
PAHs – polycyclic aromatic hydrocarbons
HOC – hydrophobic organic compounds

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of hydrophobic organic pollutants containing more than two aromatic rings in a structure. Increasing in the last decades humans activity including development of heavy industry, exploitation of crude oil and the process of incomplete combustion of organic matter in municipal and residential sectors contributed to the imbalance in nature and the accumulation of PAHs in various environmental components, even in an environment of agricultural soils. According to the Institute of Soil Science and Plant Cultivation (Puławy, Poland), 8,3% of agricultural soils is contaminated by PAHs [1]. Polycyclic aromatic hydrocarbons are characterized by mutagenic, carcinogenic, teratogenic and genotoxic properties. Due to the possibility of xenobiotics impact on

agricultural products, soils with higher than permissible levels of PAHs should be excluded from food production especially demanding (eg. for infants) and root crops. Moreover, studies have shown that high levels of polycyclic aromatic hydrocarbons may lead to inhibition of plant growth and unfavorable changes in yielding. [2].

Chemical and physical properties of soils determine the processes occurring inside, including degradation and accumulation of pollutants of anthropogenic origin. It is generally accepted that the sorption of hydrophobic organic compounds (HOC) plays a key role in their movement and determines the bioavailability. According to Oleszczuk [4] sorption processes result in immobilization of organic xenobiotics and thus limits their physicochemical and biological degradation [3]. An important factor, which determines the kinetics of sorption processes, is organic matter in soil. The functional groups in organic matter (-OH, -COOH, $-NH_2$, $-OCH_3$, =NH) determine the ability to interact with HOC. The weakly polar humic substances exhibit a very strong affinity for the hydrophobic xenobiotics. [4]. Other studies also indicate the importance of the mineral fraction of soils in the process of PAHs accumulation. The sorption properties of minerals depend on their crystal structure. The most important mineral group is clay minerals composed of alternating tetrahedral and octahedral layers. The layers are binded with each other via oxygen bridges (Al-O-Si), which create packages separated by a free space. Such expanded three-dimensional structure of the minerals is responsible for their molecular sieve properties, which guarantee excellent adsorption of water molecules [5].

The aim of the study was to evaluate the effect of the addition of commercial organic-mineral fertilizer containing humic acids and clay fraction content on immobilization of selected polycyclic aromatic hydrocarbons: phenanthrene, and in soil model systems.

## 2. Materials and methods

### 2.1. Experimental setup

The sorption was carried out in column systems with a diameter of 4 cm. As a stationary phase, silica sand with addition of various amounts of montmorillonite (Sigma Aldrich) was applied. Moreover, the addition of various amounts of organic-mineral fertilizer in the form of humic acids commercially available (according to the manufacturer, 1kg fertilizer corresponds to 30 kg of humic acids contained in manure) was used. The aqueous phase was represented by the aqueous solution of phenanthrene (Sigma Aldrich) at a concentration of 0,5 mg/l added in an amount of 200 ml. The experiment was performed in triplicate samples. In order to eliminate the degrading effect of autochthonous microorganisms, all samples were sterilized before the addition of humic acids and PAHs.

The characteristics of each system are shown in Table 1 and Table 2.

The sorption was carried out for 24 h. In order to quantification of PAHs adsorbed (x), conversion percentage were used:

$$x = \frac{a-b}{a} * 100\%,$$

where:

a – phenanthrene concentration in the initial solution (0,5 mg/l), b – phenanthrene concentration in the eluate ($mg \cdot l^{-1}$).

Table 1. The list of experimental variants
*Tab. 1. The list of experimental variants*

| Sample | Quartz sand [g] | Aqueous solution of phenanthrene (0,5 mg/l) | Humic acids [g] | Montmorillonite [g] |
|---|---|---|---|---|
| **R0** | 40,0 | + | 0,0 | 0,0 |
| **H1** | 39,5 | + | 0,5 | 0,0 |
| **H2** | 39,0 | + | 1,0 | 0,0 |
| **H3** | 38,0 | + | 2,0 | 0,0 |
| **M1** | 39,5 | + | 0,0 | 0,5 |
| **M2** | 39,0 | + | 0,0 | 1,0 |
| **M3** | 38,0 | + | 0,0 | 2,0 |
| **HM1** | 39,0 | + | 0,5 | 0,5 |
| **HM2** | 38,0 | + | 1.0 | 1,0 |
| **HM3** | 36,0 | + | 2,0 | 2,0 |

*Source: own work / Źródło: opracowanie własne*

The quantitative analysis of phenanthrene in the eluate, were carried out using the photoluminescence method (Hitachi F-7000) with the previously developed calibration curves.

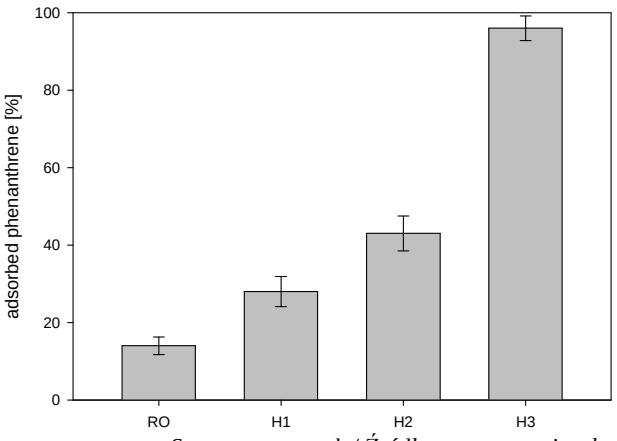
### 2.2. Statistical analysis

All analyses were replicated at least three times. Standard errors of the mean were calculated.

## 3. Results and discussion

In all experimental variants, phenanthrene concentration in the eluent decreased compared to the concentration in the initial solution. In the reference sample R0 the phenanthrene concentration of 0.43 $mg \cdot l^{-1}$ was noted, which corresponds to 86% initial concentration. Sorption properties of pure quartz sand were also confirmed by other researchers [6, 7].

Effect of humic acids on the adsorption properties of the soil model system is shown in Fig. 1. Obtained results show a clear trend of increasing sorption properties with an increase in the humic acids content.

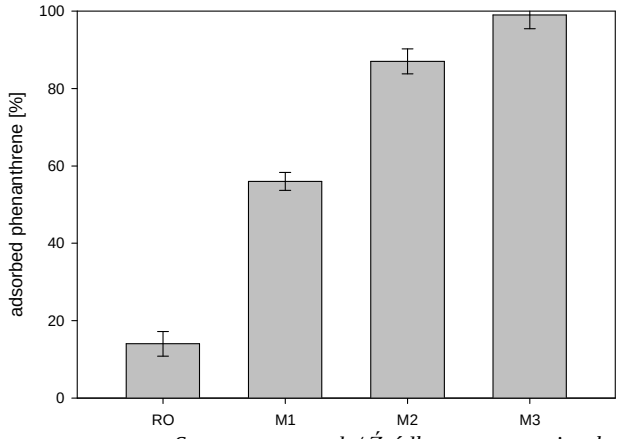



*Source: own work / Źródło: opracowanie własne*

Fig. 1. The adsorption of phenanthrene in systems with different humic acids content (names of samples in Tab. 1)
*Fig. 1. The adsorption of phenanthrene in systems with different humic acids content (names of samples in Tab. 1)*

According to Kurpińska [8], strong sorption properties of humic acids may result from hydroxy, methoxy, methyl, methylene, carboxyl, ketone, and quinone functional groups within them [8]. Studies indicate that humic substances with dominance of aromatic fractions show a very strong affinity for the hydrophobic organic substances [4]. Sorption of polycyclic aromatic hydrocarbons by organic matter was also confirmed by Chefetz et al. [9]. Furthermore Lahlou and Ortega-Calvo [11] shows that the biodegradation of polycyclic aromatic hydrocarbons in soils with a high content of organic matter may occur with less efficiency [10]. Our experience confirms this thesis pointing to the fact that the high content of humic acids with high adsorption properties causes immobilization and reduces their participation in the aqueous phase. Due to the fact that microorganisms have the ability to mineralization of PAHs in the form soluble in water, it can be concluded that the high content of humic acids can significantly reduce the rate of biodegradation, which is going to be the subject of further research.

Effect of the clay fraction content to adsorption properties is shown in Fig. 2. There is a clear tendency to increase adsorption properties with increasing the clay fraction. 5% clay fraction in the system has reduced the phenanthrene concentrations in eluate up to 5000 ng/l which corresponds to 99% sorption.

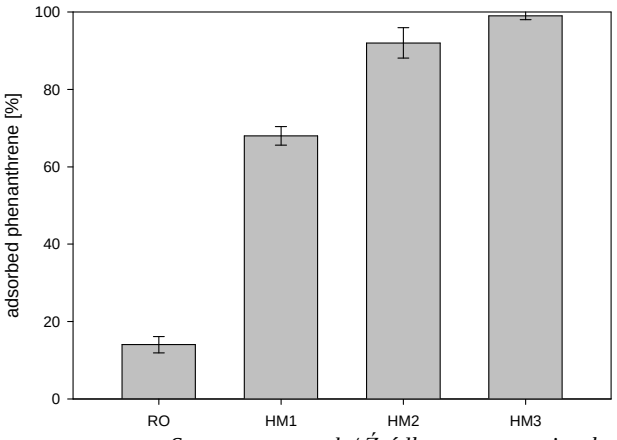



*Source: own work / Źródło: opracowanie własne*

Fig. 2. The adsorption of phenanthrene in systems with different clay content (names of samples in Tab. 1)
*Fig. 2. The adsorption of phenanthrene in systems with different clay content (names of samples in Tab. 1)*

Strong sorption properties of montmorillonite belonging to the clay minerals can be explained by the specific structure. Montmorillonite consists of two tetrahedral layers and one octahedral layer with unsaturated electric charge. Because of the low charge density per unit of packet area, interlayer cations bind weakly packets with each other and therefore they can easily displace the increasing the active adsorption surface [10]. It can be assumed that the soil containing a high proportion of clay fraction have the ability to accumulate polycyclic aromatic hydrocarbons. In addition, Lahlou and Ortega-Calvo [11] highlight the limited bioavailability of polycyclic aromatic hydrocarbons in the adsorbed form [11]. This suggests that in soils with a very high sorption properties, the PAHs mineralization may occur more slowly and thus, this kind of soils are particularly susceptible to the influence of local emissions of these compounds.

Mixed systems containing both the addition of humic acids and montmorillonite showed the strongest sorption properties. The results of each test are shown in Figure 3.




*Source: own work / Źródło: opracowanie własne*

Fig. 3. The adsorption of phenanthrene in combined systems with different humic acids and clay content (names of samples in Tab. 1)
*Fig. 3. The adsorption of phenanthrene in combined systems with different humic acids and clay content (names of samples in Tab. 1)*

It is worth noting that the sorption in combined systems is not the sum of the effect of humic acids and montmorillonite addition in separated systems. This may result from the fact that humic acids are partially adsorbed on clay minerals. This phenomenon has been described in previous studies [12, 13, 14]. Jaruwong and Wibulswas [15] highlighted the high sorption properties of montmorillonite (close to 69 mg of humic acids/g adsorbent) [15]. The loading a part of sorption surfaces of montmorillonite by humic acids explains the obtained results.

Modelling studies have shown that a high content of humic acids and clay minerals in soils (characteristic of soils with high suitability for agricultural production) is associated with an increased potential for accumulation of PAHs. On the other hand, due to the immobilization of xenobiotics, this kind of soils, are less likely to transfer contamination into agricultural products. However, it should be noted that the reduction in the bioavailability of PAHs is associated with a lower rate of natural biodegradation. Therefore, the areas exposed to the PAHs should be subjected to special monitoring which could allow checking level of toxic compounds up to date.

## 4. Conclusions

The increase in the clay fraction of the soil system is the most important factor in the sorption of polycyclic aromatic hydrocarbons and thus their accumulation in the environment.

The increase in the humic acids content in the soil has a significant effect on the sorption of polycyclic aromatic hydrocarbons.

Despite of the phenomenon of humic acids partial adsorption, the increase of the the humic acids content in the soil system containing clay minerals, results in the increasing of sorption properties in relation to polycyclic aromatic hydrocarbons.

Immobilization of polycyclic aromatic hydrocarbons in soils with a high content of clay fraction and humic acids content may contribute to a slowdown in the natural biodegradation.

Due to the risk of accumulation of xenobiotics, agricultural land exposed to contamination with PAHs characterized by a high content of organic matter and clay fraction should be regularly monitored.

## 5. References


[1] IUNG w Puławach: Monitoring chemizmu gleb ornych w Polsce w latach 2010-2012 (raport końcowy) 2012. http://www.gios.gov.pl/zalaczniki/artykuly/Monitoring_sprawozd_koncowe2.pdf

[2] Chrząścik J., Szymalska M., Kluska M.: Zanieczyszczenie wybranych próbek stałych węglowodorami aromatycznymi przy trasach wylotowych z miasta Olecko. Studia Ecologiae et Bioethicae, 2007, Vol. 5: 295-304.

[3] Oleszczuk P.: Zanieczyszczenia organiczne w glebach użyźnianych osadami ściekowymi część II. Losy zanieczyszczeń w glebie. Ecological chemistry and engineering, 2007, Vol. 14: 185-198.

[4] Oleszczuk P.: Biodostępność i bioakumulacja hydrofobowych zanieczyszczeń organicznych. Część II. Sorpcja zanieczyszczeń oraz czynniki wpływające na ten proces. Biotechnologia, 2007, Vol. 1 (76): 26-39.

[5] Műller S., Totsche U., Kőgel-Knabner I.: Sorption of polycyclic aromatic hydrocarbons to mineral surfaces. European Journal of Soil Science, 2007, Vol. 58: 918-931.

[6] Smol M., Włodarczyk-Makuła M. Wółka D.: Adsorption of polycyclic aromatic hydrocarbons (PAHs) from aqueous solution on different sorbents. Civil and Environmental Engineering Reports, 2014, Vol. 13(2): 87-96.

[7] Kőgel-Knabner I., Totsche U.: Sorption and desorption of polycyclic aromatic hydrocarbons (PAHs) to individual constituents of natural and contaminated soils. http://natres.psu.ac.th/Link/SoilCongress/bdd/symp8/237-r.pdf

[8] Kurpińska I.: Problemy związane z występowaniem substancji humusowych w wodach podziemnych. Inżynieria środowiska, 2012, Vol. 28: 55-72.

[9] Cheftez B., Deshmukh P., Hatcher E., Guthrie E.: Pyrene sorption by natural organic matter. Environmental science & technology, 2000, Vol. 34: 2925-2930.

[10] Fąfara Z., Borysławska E.: Badania laboratoryjne sorpcji produktów naftowych w gruntach ilastych. Wiertnictwo Nafta Gaz, 2011: Vol. 28: 137-147.

[11] Lahlou M., Ortega-Calvo J.: Bioavailability of labile and desorption-resistant phenanthrene sorbed to montomrillonite clay containing humic fractions. Environmental Toxicology and Chemistry, 1999, Vol. 18: 2729-2735.

[12] Liu A., Gonzalez R.: Adsorption/desorption in a system consisting of humic acid, heavy metals and clay minerals. Journal of colloid and interface science, 1999, Vol. 218: 225-232.

[13] Fitch A., Du J.: Solute transport in clay media: Effect of humic acids. Environmental Science and Technology, 1996, Vol. 30: 12-15.

[14] Rothe J., Denecke M., Dardene K.: Soft X-ray spectromicroscopy investigation of the interaction of aquatic humic acid and clay colloids. Journal of Colloid and Interface Science, 2000, Vol. 231: 91-97.

[15] Jaruwong P., Wibulswas R.: Influence of organo-clay's carbon number on the adsorption of humic acid. Asian Journal on Energy & Environment, 2003, Vol. 4: 41-59.



***The work was supported by the Polish Ministry of Science and Higher Education as project No 507.771.55.***