Magdalena BANACH-SZOTT<sup>1</sup>, Bożena DĘBSKA and Grzegorz MROZIŃSKI

# DECOMPOSITION RATE OF ANTHRACENE, FLUORENE, PYRENE AND CHRYSENE IN *LUVISOLS*

## SZYBKOŚĆ ROZKŁADU ANTRACENU, FLUORENU, PIRENU I CHRYZENU W GLEBACH PŁOWYCH

**Abstract:** The aim of the paper was to determine the stability and intensity of decomposition of selected polycyclic aromatic hydrocarbons (PAHs) (anthracene, fluorene, pyrene, chrysene) in *Luvisols*. The study was carried out based on soil samples representative of the Kujawsko-Pomorskie Region, collected from areas exposed to and protected from direct contamination with PAHs. Soil samples were polluted with selected PAHs at the amount corresponding to 10 mg PAHs/kg. The PAHs-polluted soil samples were incubated for 10, 30, 60, 120, 180 and 360 days at the temperature of 20–25 °C and fixed moisture – 50 % of field water capacity. In this work High Performance Liquid Chromatography (HPLC) was applied. It was found that majority of PAHs decomposed within first 30 days of the experiment. Decomposition of fluorene and anthracene was much faster than for pyrene and chrysene. The lowest rate of PAHs decomposition was noted for the samples of the soil with the highest content of organic carbon, carbon of the fractions of humic acids and humins, which clearly points to an essential role of organic matter in the PAHs sorption processes.

Keywords: PAHs, HPLC, Luvisols

## Introduction

Soil is an element of the natural environment in which there accumulates most hydrophobic organic pollutants, including polycyclic aromatic hydrocarbons (PAHs) [1]. PAHs are organic compounds which include from two to a dozen or so aromatic rings. The structures of respective PAHs differ in the pattern of benzene rings in the molecule and all the connected rings have two common carbon atoms. Ring bonds can occur in various spatial patterns: linear (*eg* anthracene, tetracene), cluster (*eg* pyrene, perylene) and angular pattern (phenanthrene, tetraphen) [2]. In general, PAHs, due to their specific physicochemical properties and the resultant low susceptibility to degradation are considered to be the so-called stable organic pollutants [3, 4].

<sup>&</sup>lt;sup>1</sup> Department of Environmental Chemistry, University of Technology and Life Sciences, ul. Bernardyńska 6, 85–029 Bydgoszcz, Poland, phone: +48 52 374 95 11, fax: +48 52 374 95 05, email: magdybe@poczta.fm, debska@utp.edu.pl

PAHs which occur in the soil environment can be of autogenic origin (formed as a result of humification) and exogenous, connected with the deposition of particulate matter from burning fossil fuels and biomass [5]. With that in mind, their presence ranges a lot, depending on the location, the type and method of soil use. The highest PAHs level (20000  $\mu$ g/kg) is reported in the soils of big cities, along the roads, in the vicinity of industrial plants [6–9], while in the soils of arable fields, meadows and other agricultural land it usually does not exceed 100–400  $\mu$ g/kg [3, 4, 10, 11].

According to Bojakowska and Sokolowska [12], the composition and amount of PAHs in soil is a derivative of two parallel processes which occurs in soil. The first one is the formation of new compounds as a result of the deposition of PAHs from the anthropogenic sources and the degradation of organic remains, while the second process covers a microbiological degradation of hydrocarbons which occurs with the participation of fungi, bacteria and Actinobacteria [13–15]. Interestingly, microbiological processes are the only way of a complete PAHs decomposition in the soil environment. PAHs in soils also undergo abiotic transformations, namely sorption, leaching, reactions with other compounds and photodegradation [6, 10, 16–19].

One of the key parameters affecting the amount of PAHs in soil is the content of organic matter. Organic matter shows a high sorption potential, and the stability of hydrocarbons in soil depends considerably on that process. As a result of sorption their mobility and PAHs availability to microorganisms decrease [20–22]. For the processes of PAHs sorption by organic matter not only its total content but also its quality composition are very important [23–26]. In general it is assumed that humins show a much greater sorption capacity towards PAHs than humic acids which, in turn, can sorb those hydrocarbons stronger than fulvic acids [26, 27].

Discussing PAHs transformations in soil, one shall note such factors as moisture, pH, temperature, oxygen access. PAHs demonstrate the highest stability in the air-dry soils (1 % field water capacity). The decomposition of PAHs is most intensive in the soils of the moisture falling within the range of 50 to 65 % field water capacity. In the soils of a higher water content (moisture above 65 % field water capacity) there is observed another decrease in the PAHs decomposition rate [28–30].

Yet another factor affecting the hydrocarbons decomposition intensity is temperature. The temperature optimal for bacteria and fungi decomposing PAHs is 1538 °C. Below the thermal optimum there occurs an inhibition of growth and soil microflora activity and a decrease in the biochemical reactions rate leading to the decomposition of PAHs [30–32].

The soil reaction, in turn, affects both the PAHs sorption processes and its biological activity. In the acid soils there is observed an increase in the intensity of the sorption process, and thus, a slow-down in the biological transformations of PAHs [23, 33–35]. The pH optimal for PAHs-decomposing microorganisms is 6.5–7.5. Although fungi develop well in the environment showing a slightly acid reaction (pH 4.5–6.0), the key role in the PAHs decomposition is played by bacteria. For that reason in the soils of low pH there occurs a decrease in the decomposition rate of those compounds, caused by a decreased activity of microorganisms.

The PAHs stability in soil also depends on the structure and the properties of hydrocarbons only. It was found that the higher the number of rings in the compound,

and thus the higher the molecular weight, the lower the decomposition rate, which is related to an increased PAHs hydrophobicity and a strong adsorption by soil as well as the fact that they are more resistant to the microbiological attack [27, 36, 37].

The aim of the paper was to determine the stability and intensity of decomposition of selected polycyclic aromatic hydrocarbons (PAHs) (anthracene, fluorene, pyrene, chrysene) in *Luvisols*.

## Materials and methods

#### **Research material**

The research was performed based on the *Luvisols* representative for the Region of the Kujawy and Pomorze, taken from the areas exposed to a threat and not exposed to any such threat of direct pollution with PAHs. The following soils were considered: samples number 3, 4 - sampled from the location of Bielawy (the soil exposed to a threat (3) and not exposed to any such threat (4) of direct effect of PAHs); sample number 5 - Orlinek (soil not exposed to the threat of PAHs pollution); sample number 7 - Slesin in the vicinity of Bydgoszcz (soil exposed to the effect of PAHs). The basic properties of soils used in the experiment are given in Table 1.

Table 1

Communic	Percentage	e share of resp ctions	bective fra-	TOC	C <sub>HUMIN</sub>			
Sample	2–0.05 mm	0.05–0.002 mm	> 0.002 mm			[g/kg]		
Luvisol (Lu3W)	82	18	0	12.80	0.66	3.906	2.094	5.546
Luvisol (Lu4W)	84	11	5	6.63	0.50	2.543	1.657	1.780
Luvisol (Lu5W)	75	19	6	11.74	1.03	3.424	2.906	4.388
Luvisol (Lu7W)	64	26	10	13.77	1.26	4.835	2.645	5.482

The granulometric composition of the soils, the content of total organic carbon (TOC) and nitrogen  $(N_t)$  as well as the content of respective fractions of organic carbon

Soil samples were polluted with selected PAHs (fluorene, anthracene, pyrene and chrysene), at the amount corresponding to 10 mg PAHs/kg. The PAHs-polluted soil samples were incubated for 10, 30, 60, 120, 180 and 360 days at the temperature of 20–25 °C and fixed moisture (50 % of field water capacity).

After the completion of incubation, the samples were dried at room temperature were mixed and sieved.

#### Determining the PAHs content in soil

The content of PAHs (fluorene, anthracene, pyrene and chrysene) was determined in the samples of initial soils and after 10, 30, 60, 120, 180 and 360 days with the use of High Performance Liquid Chromatography. PAHs from the soils were extracted with cyclohexane applying the Soxhlet apparatus. The extracts were evaporated to dryness, and the rest was solved in 4  $cm^3$  acetonitrile (ACN).

The chromatographic separation of PAHs-containing solutions was made using the liquid chromatograph HPLC Series 200 provided by Perkin-Elmer equipped with a DAD (absorption) and FL (fluorescence) detector. There was applied an analytic column to separate PAHs provided by Waters of the particle size of 5  $\mu$ m and 250 · 4.6 mm in size. The mobile phase was composed of eluent A: H<sub>2</sub>O and eluent B: ACN. There was used a gradient separation program of a varied flow rate. The initial composition of the mobile phase was 70 % of eluent B and its concentration was growing linearly in the analysis time. Gradient was completed after 34 min when the content of eluent B was 100 %.

The extracts of the unpolluted (initial) soil samples were analysed with the fluorescence detector applying excitation wavelength  $\lambda_{ex} = 250$  nm and emissions  $\lambda_{em} = 405$  nm. The injection was 10 mm<sup>3</sup>.

The extracts of the samples of soils polluted with PAHs, incubated 10, 30, 60, 120, 180 and 360 days were analysed with the absorption detector. The detection was made at  $\lambda = 254$  nm. The injection was 100 mm<sup>3</sup>.

The qualitative analysis of respective hydrocarbons was made with a comparison of soil extracts chromatograms with the model mixtures chromatograms.

The quantitative assays of fluorene, anthracene, pyrene and chrysene were made based on their model curves.

### Results

The basic properties of the soil sampled from the sites exposed to and non-exposed to a direct effect of PAHs are given in Table 1. The highest content of total organic carbon (TOC), total nitrogen (Nt) and the share of fine fraction was found for *Luvisol* (Lu7W). The lowest content of TOC and Nt was reported for the soil sampled at Bielawy – Lu3W.

The contents of PAHs recorded for the initial samples of soils from the sites located close to transport routes (Lu3W and Lu7W) and away from them (Lu4W and Lu5W) are given in Table 2.

Table 2

G 1	Fluorene	Anthracene	Pyrene	Chrysene	Sum
Sample			[µg/kg]		
Lu3W	57.1	0.94	7.39	24.1	89.5
Lu3W'	2557	2501	2507	2524	10090
Lu4W	4.00	1.08	6.45	9.80	21.3
Lu4W'	2504	2501	2506	2510	10021
Lu5W	15.1	2.15	9.70	7.14	34.1
Lu5W'	2515	2502	2510	2507	10034
Lu7W	193	15.7	246	99.0	553
Lu7W'	2693	2516	2746	2599	10553

Contento or rritio in the boll buildie	Contents	of	PAHs	in	the	soil	sample
--	----------	----	------	----	-----	------	--------

It was shown that the highest contents of the PAHs analyzed (anthracene, pyrene, chrysene and fluorene) were recorded for soil sample Lu7W, exposed to a direct effect of PAHs, while the soil sampled from the sites away from transport routes (Lu4W, Lu5W) showed the lowest PAHs contents, except for anthracene the lowest content of which was recorded for sample Lu3W.

#### Changes in the content of selected PAHs during incubation

The changes in the PAHs content reported for the *Luvisol* sampled at Bielawy in the vicinity of the transport route (Lu3) are given in Fig. 1 (sample Lu3W' refers to soil sample Lu3W additionally polluted with 4 selected PAHs (fluorene, anthracene, pyrene and chrysene), however, the amount of each of the PAHs was 2500  $\mu$ g/kg). It was demonstrated that the contents of fluorene, anthracene, pyrene, chrysene in the samples decreased with the incubation time (Fig. 1). The highest decrease in PAHs, as compared with the initial content, was recorded for the sample after 10 days of incubation for which there was recorded a 64.6 % decrease in the initial content of fluorene, a 89.7 % decrease in the content of anthracene and by 59 % – pyrene. Over the 1<sup>st</sup> 10 days of incubation the lowest decrease was noted for chrysene – 28.7 % of its initial content. Over the successive periods of incubation: 10–30 and 30–60 days, the amount of chrysene which underwent decomposition accounted for 25.8 % and 31.2 % of its initial content, respectively. The lowest PAHs contents were recorded for the soil samples after 360 days of the experiment. The content of fluorene accounted for 3.8 % of its initial content, anthracene – 1.2 %, pyrene – 8.3 % and chrysene 9 %.



Fig. 1. Changes in the content of selected PAHs during incubation in the soil sampled at Bielawy (\* - Lu3W - initial soil, Lu3.1 - after 10 days of incubation, Lu3.2 - 30 days, Lu3.3 - 60 days, Lu3.4 - 120 days, Lu3.5 - 180 days, Lu3.6 - 360 days

In the *Luvisol* sampled also at Bielawy (Lu4) (Fig. 2), however, at the sampling site away from the transport route, the amount of the decomposed PAHs over the first 10 days of incubation was higher than in soil samples Lu3 (Fig. 1). At the first stage of incubation in soil samples Lu4 91.6 % anthracene, 88.5 % fluorene, 72.7 % pyrene and 48.3 % chrysene was decomposed, as compared with their initial contents. The lowest PAHs contents were reported for the samples of soils after 360 days of the experiment: as for fluorene – 3.1 % of the initial content, anthracene – for 1.1 %, pyrene –for 6.3 %, and chrysene – for 7.1 %.



Fig. 2. Changes in the content of selected PAHs during incubation in the soil sampled at Bielawy (\* - denotation as in Fig. 1)

The contents of fluorene, anthracene, pyrene, chrysene during the incubation in *Luvisol* sampled at Orlinek are given in Fig. 3. After the first 10 days of incubation the highest decrease was recorded for fluorene – 82.7 % of its initial content and anthracene – 85.1 %. The decrease in the content of pyrene and chrysene was much lower and it accounted for 56.7 % for pyrene and 41.8 % for chrysene. There was noted, however, a high decrease in those PAHs from the 11<sup>th</sup> to the 30<sup>th</sup> day of incubation (for chrysene by 77.3 %, and for pyrene by 77.9 % of the initial content). Finally, after 360 days of the experiment, the content of fluorene accounted for 3.3 % of its initial content, anthracene – 1.2 %, pyrene 6.2 % and chrysene – 7.2 %.

The changes in the content of the PAHs investigated in the *Luvisol* sampled at Slesin (Lu7) are broken down in Fig. 4. At the first stage of the experiment, for the first 10 days, there was reported the highest decrease in the content of anthracene (65.8 % of the initial content), while as for fluorene, pyrene, and chrysene, the highest decrease was recorded 30 days after the start of the experiment, respectively by 70.6 %, 45.6 % and 45.1 % of their initial content. The amount of PAHs which remained non-



Fig. 3. Changes in the content of selected PAHs during incubation in the soil sampled at Orlinek (\* - denotation as in Fig. 1)

-decomposed after 360 days of incubation was as follows: for anthracene -2.3 % of the initial content, for fluorene -3.6 %, for pyrene -6.3 %, and for chrysene 8.6 % (Fig. 4).



Fig. 4. Changes in the content of selected PAHs during incubation in the soil sampled at Slesin v/Bydgoszcz (\* - denotation as in Fig. 1)

The content of the sum of the PAHs investigated in the *Luvisol* samples during the incubation is given in Table 3. After the first 10 days of the experiment the highest

decrease in the content of the sum of PAHs was noted for soil sample Lu4 – 75.3 % of the initial content. The lowest decreases in the sum of PAHs (60.5 % and 66.6 %) were recorded for soil samples Lu3 and Lu5, respectively. As for soil sample Lu7, on the other hand, there was noted only a 28.4 % decrease in the contents of the sum of PAHs. Once the incubation was completed, the content of the sum of PAHs in the soil sampled at Bielawy and at Orlinek was higher than its initial content (Table 3). In the soil sampled at Slesin after 360 days, the content of the sum of PAHs was similar to its initial content.

Table 3

Samula	Sum [µg/kg]								
Sample	Lu3	Lu4	Lu5	Lu7					
W	89.5	21.3	34.1	553					
W'	10090	10021	10034	10553					
10 days	3990	2479	3352	7558					
30 days	2903	1671	1564	3928					
60 days	2064	1315	1141	2849					
120 days	1379	1090	715	2109					
180 days	1032	684	543	1320					
360 days	563	440	449	552					

Content	of	the	sum	of	PAHs	during	the	incubation
---------	----	-----	-----	----	------	--------	-----	------------

Table 4 presents the times of partial PAHs decomposition for two stages (0-30 days) and 30-180 days) and for the entire incubation period (0-360 days).

Table 4

PAHs	Period	Lu3	Lu4	Lu5	Lu7
	0-30	12.63	9.04	9.59	17.00
Fluorene	30-180	92.42	117.98	94.08	111.4
	0–360	76.47	71.46	73.16	75.04
	0-30	8.23	8.15	7.54	8.45
Anthracene	30-180	77.25	58.61	72.2	20.4
	0–360	56.9	55.18	56.86	66.27
	0-30	19.73	15.74	13.76	34.16
Pyrene	30-180	92.7	123.33	108.22	58.28
	0–360	100.2	90.27	89.59	90.24
	0-30	32.6	13.79	14.04	34.68
Chrysene	30-180	113.8	135.4	98.3	140
	0-360	103.39	94.28	94.72	101.78
	0-30	16.69	11.61	11.19	21.04
Sum	30-180	100.51	116.38	98.26	95.32
	0-360	86.44	79.82	80.30	84.55

Partial decomposition time  $(T_{1/2})$  – PAHs in soils at various experiment stages

At the initial stage there were noted the lowest values of the partial PAHs decomposition, which means that the transformations of hydrocarbons over that period were most intensive. The highest decomposition rate was recorded for anthracene; the lowest values of the partial decomposition time in the soil samples, whereas the lowest rate was noted for chrysene for which the highest  $T_{1/2}$  values were recorded. Interestingly, over that period fluorene, anthracene, pyrene and chrysene were undergoing the slowest transformations in the case for the soil sample exposed to a direct effect of PAHs, sampled at Slesin (Lu7). Throughout the incubation period, similarly as over the first 30 days, the highest decomposition rate was noted for anthracene (the lowest values of parameter  $T_{1/2}$ ).

#### Discussion

The content of PAHs in soils was determined by the sampling site. In the soils not exposed to a direct effect of PAHs there were noted low contents of those compounds (Table 2). Similar relations were reported by Adamczewska et al [8] and Zerbe et al [11]. Higher PAHs contents were recorded for the soil sampled in the close vicinity of the transport route, namely exposed to a direct effect of those compounds. A few-fold higher PAHs contents in soils exposed to intensive effects of transport coincide with the results reported by Adamczewska et al [8] and Kluska and Kroszczynski [9]. Weiss et al [13] and Wilcke and Amelung [19] report that high contents of such PAHs as anthracene, pyrene or chrysene point to an intensive human impact on the environment.

Interestingly, soil sample Lu3W sampled at the site exposed to a direct effect of PAHs showed lower PAHs content than soil sample Lu7W, also sampled at the site exposed to a direct effect of PAHs (Table 2), which demonstrates a moderate anthropopressure for soil Lu3W.

In all the soils investigated the highest decomposition of the compounds analysed occurred over the first 10 days of the experiment and then from the 11<sup>th</sup> to the 30<sup>th</sup> day of incubation (Figs 1–4). Similar relationships were reported by Maliszewska-Kordybach [35] demonstrating the highest PAHs losses in the first 30 days of soil sample incubation. According to Maliszewska-Kordybach [30, 33] and Maliszewska-Kordybach and Masiak [34], such high decreases in the PAHs content at the first decomposition stages are mostly due to microbiological processes. The reason of such a fast decomposition of the hydrocarbons analysed at the initial period of incubation by soil microorganisms are the experimental conditions: moisture: 50 % of field water capacity, temperature 20–25 °C. As reported by Bossert and Bartha [28] as well as Maliszewska-Kordybach [29], soil moisture ranging from 37 to 65 % of field water capacity creates optimal conditions for the development of soil microflora participating in the decomposition of PAHs. Whereas 15–38 °C is the temperature optimal for bacteria and fungi which take part in PAHs decomposition [30–32].

A fast decomposition at the initial stage of the experiment was observed for fluorene and anthracene, as compared with pyrene and chrysene, which is due to the fact that the rate of microbiological decomposition is higher for the compounds of a lower molecular weight and a lower number of aromatic rings. According to Maliszewska-Kordybach [33] 3-ring fluorene and anthracene can be not only decomposed but also used by bacteria as the source of carbon and energy.

As for fluorene and anthracene, a high decrease in their content over the first 30 days of incubation can be due to abiotic transformations which are a result of chemical oxidation, photodegradation, sorption, oxidation and leaching [16, 33]. Interestingly, however, the conditions of the experiment made the photodegradation and leaching impossible. One can assume that in their case it was oxidation which triggered considerable soil loss mechanism, which is seen from the physicochemical properties of those compounds. Henry's constants for fluorene and anthracene fall within the range  $10^{-5} < H < 10^{-3}$  atm/mol/m<sup>3</sup> classified as the range for compounds of moderate volatility [16].

A high stability of pyrene and chrysene in the soil samples is connected with their low susceptibility to oxidation, which is seen from a low vapour pressure and low solubility in water [2]. Other causes of high resistance of those compounds to the processes of decomposition can be found in their structure. The pattern of pyrene and chrysene rings shows a high thermodynamic stability [16]. A greater stability of 4-ring hydrocarbons is also due to their stronger sorption by organic matter which, as a result, limits the bioavailability of those PAHs. The lowest intensity of decomposition among the PAHs was recorded for chrysene, a compound of the highest molecular weight.

The coefficients of correlation recorded between the time of partial PAHs decomposition and the content of TOC, the content of  $C_{HAs}$  and  $C_{HUMIN}$  show that the intensity of decomposition of fluorene, anthracene and chrysene was also determined by soil properties (Table 5). The lowest decomposition rate for the first 30 days was found for soil sample Lu7 of the highest, of all the soils, content of organic carbon, carbon of the fraction of humic acids and humins (Table 1). The above relationships confirm the role played by organic matter in PAHs sorption processes. Many authors [3, 21, 22, 30] claim that PAHs sorption by the organic soil fraction is the basic process determining the activity and the bioavailability of hydrocarbons in the soil environment.

Table 5

Demonstern	Fluorene	Anthracene	Pyrene	Chrysene	Sum
Parameter			$T_{1/2}$ for 0–30 days		
TOC [g/kg]	0.749			0.757	0.711
C <sub>HAs</sub> [g/kg]	0.946		—	0.868	0.911
C <sub>HUMIN</sub> [g/kg]	0.723	—	—	0.799	0.708
			$T_{1/2}$ for 0–360 days	3	
TOC [g/kg]	0.852	0.658		0.744	0.732
C <sub>HAs</sub> [g/kg]	0.775	0.886	—	0.788	0.740
C <sub>HUMIN</sub> [g/kg]	0.921	0.578	—	0.813	0.812

Significant values of the coefficients of correlation between the time of partial PAHs decomposition and selected parameters defining soil properties

The PAHs stability investigated in all the *Luvisol* samples was increasing in the following order: chrysene > pyrene > fluorene > anthracene.

## Conclusions

1. The contents of PAHs (fluorene, anthracene, pyrene and chrysene) in the samples of soils additionally unpolluted with PAHs depend on the sampling site. Higher PAHs contents were recorded for the soil sampled in a close vicinity of the transport route, as compared with the soil sampled away from the transport route.

2. The decomposition rate of PAHs introduced into soils depended on the experiment duration. The PAHs degradation process was most intensive for the first 30 days of incubation.

3. The PAHs decomposition intensity at the initial stage of incubation depended on the PAHs properties. A higher decomposition rate, as compared with pyrene and chrysene, was noted for anthracene and fluorene, as the compounds of a lower molecular weight and a lower number of aromatic rings.

4. The lowest PAHs decomposition rate was recorded for the samples of soil with the highest content of organic carbon, carbon of the fraction of humic acids and humins, which clearly points to an essential role of organic matter in PAHs sorption processes.

#### Acknowledgement

The research has been made as part of N N310 3123 34 research project, financed by the Ministry of Science and Higher Education.

#### References

- Kluska M. Dynamika sorpcji wielopierścieniowych węglowodorów aromatycznych przez glebę w pobliżu dróg o dużym natężeniu ruchu komunikacyjnego. Arch Ochr Środow. 2004;2:83-93.
- [2] Bojakowska I. Charakterystyka wielopierścieniowych węglowodorów aromatycznych i ich występowanie w środowisku. Biuletyn PIG. 2003;405:5-28.
- [3] Wild SR, Jones KC. Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget. Environ Pollut. 1995;88(1):91-108.
- [4] Maliszewska-Kordybach B. Zależność między właściwościami gleby i zawartością w nich WWA; na przykładzie gleb z terenu użytków rolnych w województwie lubelskim. Arch Ochr Środow. 1998;3:79-91.
- [5] Lichtfouse E, Budziński H, Garrigues P, Eglinton T. Ancient polycyclic aromatic hydrocarbons in modern soils:<sup>13</sup>C, <sup>14</sup>C and biomarker evidence. Org Geochem. 1997;26(5-6):353-359.
- [6] Wilcke W, Amelung W, Zech W. Heavy metals and polycyclic aromatic hydrocarbons (PAHs) in a rural community leewards of a waste incineration plant. Z Pflanzenernahr Bodenk. 1997;160(3):369-378.
- [7] Wcisło E. Soil contamination with polycyclic aromatic hydrocarbons (PAHs) in Poland a review. Pol J Environ Stud. 1998;7(5):267-272.
- [8] Adamczewska M, Siepak J, Gramowska H. Studies of levels of polycyclic aromatic hydrocarbons in soils subjected to anthropic pressure in the City of Poznań. Pol J Environ Stud. 2000;9(4):305-321.
- [9] Kluska M, Kroszczyński W. Zawartość niektórych policyklicznych węglowodorów aromatycznych w pobliżu dróg o dużym nasileniu ruchu. Chem Inż Ekol. 2000;7:563-573.
- [10] Menzie CA, Potocki BB, Santodonato J. Exposure to carcinogenic PAHs in the environment. Environ Sci Technol. 1992;26(7):1278-1284.
- [11] Zerbe J, Sobczyński T, Siepak J. Zanieczyszczenia gleby w ogródkach działkowych metalami ciężkimi i wielopierścieniowymi węglowodorami aromatycznymi. Przyroda i Człowiek. 1995;8:5-16.
- [12] Bojakowska I, Sokołowska G. Tło geochemiczne wielopierścieniowych węglowodorów aromatycznych (WWA) w glebach leśnych. Przegl Geolog. 1998;46(10):1083-1085.

- [13] Weiss PA, Riss E, Gschmeidler E, Schentz H. Investigation of heavy metal, PAHs, PCB patterns and PCDD/F profiles of soil samples from an industrialized urban area (Linz, Upper Austria) with multivariate statistical methods. Chemosphere. 1994;29:2223-2236.
- [14] Ollivon D, Garbon B, Chesterikoff A. Analysis of distribution of some polycyclic aromatic hydrocarbons in sediments and suspended matter in the river Seine (France). Water, Air, Soil Pollut. 1995;81(1-2):135-152.
- [15] Sutherland JB, Rafii F, Khan AA, Cerniglia CE. Mechanisms of polycyclic aromatic hydrocarbon degradation. [In:] Microbial Transformation and Degradation of Toxic Organic Chemicals. Young LY, Cerniglia CE, editors. New York: Wiley-Liss; 1995:269-306.
- [16] Maliszewska-Kordybach B. Udział procesów abiotycznych w stratach 3- i 4-pierścieniowych węglowodorów aromatycznych z gleb. Rocz Glebozn. 1991;42(1-2):69-78.
- [17] Mahmood SK, Rao PR. Microbial abundance and degradation of polycyclic aromatic hydrocarbons in soil. Bull Environ Contam Toxicol. 1993;50:486-491.
- [18] Kurek E, Stec A, Staniak D. Bioremediacja ex situ gleby skażonej produktami ropopochodnymi. Ekoinżynieria. 1998;9:5-11.
- [19] Wilcke W, Amelung W. Persistent organic pollutants in native grassland soils along a eliosequence in North America. Soil Sci Soc Amer J. 2000;64:2140-2148.
- [20] Bauer JE, Capone DG. Degradation and mineralization of the polycyclic aromatic hydrocarbons anthracene and naphtalene in intertidal marine sediments. Appl Environ Microbiol. 1985;50(1):81-90.
- [21] Jensen KC, Folker-Hansen H. Soil quality criteria for selected organic compounds. NERI Report. 1995;47:117-130.
- [22] Cousins IT, Kreibich H, Hudson LE, Lead WA, Jones KC. PAHs in soil: contemporary UK data and evidence for potential contamination problems caused by exposure of samples to laboratory air. Sci Total Environ. 1997;203:141-156.
- [23] Chiou CT. Theoretical considerations of the partition uptake of nonionic organic compounds by soil organic matter. [In:] Reactions and movement of organic chemicals in soils. Sawhney BL, Brown K, editors. SSA Special Publication 22. Madison: Soil Science Society of America; 1989:1-29.
- [24] Weissenfelts WD, Klewer HJ, Langhoff J. Adsorption of polycyclic aromatic hydrocarbons (PAHs) by soil particles: influence on biodegradability and biotoxicity. Appl Microbiol Biotechnol. 1992;36(5):689-696.
- [25] Barancikova C, Gergelova Z. Soil parameters influencing of PCBs sorption. [In:] Cantaminated Soil '95. den Brink WJ, Bosman R, Arendt F, editors. Dordrecht–Boston–London: Kluwer Academic Publishers; 1995:357-358.
- [26] Maliszewska-Kordybach B. The presistence of pollutants in soil is related among other factors to their sorption. Hydrophobic Xenobiotics, eg highly carcinogenic and mutagenic polycyclic aromatic hydrocarbons (PAHs), are sorbed mainly on the organic fraction of soil. Arch Ochr Środow. 1995;2:183-190.
- [27] Maliszewska-Kordybach B. Wpływ nawożenia organicznego na trwałość wielopierścieniowych weglowodorów aromatycznych. Arch Ochr Środow. 1992;2:153-162.
- [28] Bossert ID, Bartha R. Structure biodegradability relationships of polycyclic aromatic hydrocarbons in soil. Bull Environ Contam Toxicol. 1986;37:490-495.
- [29] Maliszewska-Kordybach B. Wpływ poziomu wilgotności gleby piaskowej na zakres i szybkość rozkładu fluorenu, antracenu i pirenu. Rocz Glebozn. 1990;41:47-57.
- [30] Maliszewska-Kordybach B. Trwałość wielopierścieniowych węglowodorów aromatycznych w glebie. Rozprawa habilitacyjna. Puławy: Wyd IUNG; 1993.
- [31] Siuta J. Biodegradacja ropopochodnych składników w glebach i w odpadach. Warszawa: IOŚ; 1993.
- [32] Schlegel HG. Mikrobiologia ogólna. Warszawa: Wyd Nauk PWN; 2005.
- [33] Maliszewska-Kordybach B. Wielopierścieniowe węglowodory aromatyczne w środowisku przyrodniczym. Wiad Ekol. 1986;32(1):47-65.
- [34] Maliszewska-Kordybach B, Masiak D. Kinetyka rozkładu fluorenu w glebie piaskowej. Rocz Glebozn. 1988;39:188-199.
- [35] Maliszewska-Kordybach B. Biodegradacja wielopierścieniowych węglowodorów aromatycznych w glebach narażonych uprzednio na wpływ tych związków. Arch Ochr Środow. 1991;2:139-149.
- [36] Fudryn G, Kawala Z. Odnowa zanieczyszczonych gruntów metodami in situ. Ochr Srodow. 1996;18(2):27-34.

[37] Lisowska K, Długoński J. Biodegradacja związków ropopochodnych przez grzyby strzępkowe. Biotechnologia. 2003;63(4):92-100.

#### SZYBKOŚĆ ROZKŁADU ANTRACENU, FLUORENU, PIRENU I CHRYZENU W GLEBACH PŁOWYCH

Katedra Chemii Środowiska, Wydział Rolnictwa i Biotechnologii Uniwersytet Technologiczno-Przyrodniczy w Bydgoszczy

Abstrakt: Celem pracy było określenie trwałości i intensywności rozkładu wybranych wielopierścieniowych węglowodorów aromatycznych (fluorenu, antracenu, pirenu i chryzenu) w glebach płowych. Do badań pobrano próbki gleb reprezentatywne dla Regionu Kujawsko-Pomorskiego z terenów narażonych i nienarażonych bezpośrednio na zanieczyszczenia WWA. Próbki gleb zanieczyszczono wybranymi WWA w ilości odpowiadającej 10 mg WWA/kg. Zanieczyszczone WWA próbki gleb inkubowano 10, 30, 60, 120, 180 i 360 dni w temperaturze 20–25 °C i w stałej wilgotności – 50 % polowej pojemności wodnej. W celu oznaczenia zawartości WWA zastosowano metodykę wykorzystującą wysokosprawną chromatografię cieczową (HPLC). Stwierdzono, że najwięcej WWA rozkładało się w czasie pierwszych 30 dni prowadzenia doświadczenia, przy czym fluoren i antracen rozkładały się zdecydowanie szybciej niż piren i chryzen. Najwolniejszy rozkład frakcji kwasów huminowych i humin, co w sposób jednoznaczny wskazuje na istotną rolę materii organicznej w procesach sorpcji WWA.

Słowa kluczowe: WWA, HPLC, gleby płowe