Tomasz CIESIELCZUK<sup>1</sup>, Czesława ROSIK-DULEWSKA<sup>2</sup> and Joanna POLUSZYŃSKA<sup>3</sup>

# MIGRATION OF PAHs IN THE ARABLE LAYER OF FLOODED SOIL – MODEL EXPERIMENT

### MIGRACJA WWA W WARSTWIE ORNEJ GLEB ZALANYCH WODAMI POWODZIOWYMI – DOŚWIADCZENIE MODELOWE

**Abstract:** Soils periodically, or permanently, waterlogged and soils exposed to flood waters are heavily imperilled to pollution of inorganic and organic compounds. They are primarily compounds that are brought with the inflowing (highly loaded) floodwater and indigenously produced within the soil profile by anaerobic metabolism of the organic matter. PAHs compounds are adsorbed by the soil from the floodwaters and move in the soil profile posing a threat to groundwater. In addition, when the flood recedes, these compounds may be taken up by the crops. In this study soil pollution with polycyclic aromatic hydrocarbons (PAHs) derived from the decomposition of organic matter and silt and their migration in the arable layer of soil.

Keywords: flood, PAHs, soil, migration of pollutants

### Introduction

Polycyclic Aromatic Hydrocarbons (PAHs), due to their toxicity, mutagenicity and carcinogenicity constitute persistent organic pollutants of the environment [1–3]. They are formed through natural processes (volcanic eruptions, forest fires, decomposition of biomass) and anthropogenic (industry and transport) [2, 4]. These compounds are emitted into the atmosphere from combustion of various organic materials such as liquid and solid fossil fuels; commonly used as fuel to drive piston engines and within

<sup>&</sup>lt;sup>1</sup> Department of Land Protection, Opole University, ul. Oleska 22, 45–052 Opole, Poland, phone: +48 77 401 60 27, email: tciesielczuk@uni.opole.pl

<sup>&</sup>lt;sup>2</sup> Institute of Environmental Engineering of the Polish Academy of Sciences, ul. M. Skłodowskiej-Curie 34, 41–819 Zabrze, Poland, phone: +48 32 271 70 40, email: dulewska@ipis.zabrze.pl

<sup>&</sup>lt;sup>3</sup> Institute of Ceramics and Building Materials, ul. Oświęcimska 21, 45–641 Opole, Poland, phone: +48 77 745 32 01, email: j.poluszynska@icimb.pl

<sup>\*</sup> Corresponding author: tciesielczuk@uni.opole.pl

the energy sector [1, 2]. A huge number of sources (natural and anthropogenic) create such compounds, along with their considerable dispersion; enable PAHs to be present in all components of the environment [5–9]. PAHs are nonpolar and aromatic compounds, therefore are practically insoluble in water, but in the presence of other organic impurities their solubility may increase. Due to their high affinity to the solids, they may adsorb onto the surface of the particles and, then with them can move over large distances. Along with rainwater PAHs are absorbed on particulates and washed away from the surface of roads, parking lots, rooftops, warehouses, petrol stations, places of storage of solvents, pesticides, landfills and both get into the soil and hence into the soil profile and groundwater. In the surface reservoirs these compounds settle at the bottom, accumulating in sediments. Some of PAHs are degraded over time (weeks, months) by various groups of microorganisms, and the others may further accumulate in the food chain. PAHs are collected by the plants through the roots, and then moved to the aerial parts [10].

Long-term rainfall and rapid thaw lead to raised water stage in rivers, resulting in deluge or flood, resulting in long-term negative effects on the environment. Flooded soil sustaining even for a short time, leads to a displacement of air from the soil pores what results in formation of anaerobic conditions in their profile. Such a situation may be the case for all types of soils [11].

Pollutants that are carried along with the floodwater can be divided into two main groups. The first group consists of inorganic compounds which include, amongst others, heavy metals and nutrients, which migrate into the soil profile and are stopped on the physical, biological or chemical sorption processes [3]. The second group are the previously mentioned organic compounds that are the building blocks of pre-decomposed plant and animal residues as well as organic matter of different origins. These are originally contained in the soil, compost and manure coming from the manure, liquid manure tanks and finally septic tanks. Furthermore, the floodwaters contain organic compounds that may have toxic properties, for example: substances purifying lubricants or having irritant nature such as alcohols, hydrocarbons, including aliphatic and monoaromatic [12]. In the floodwaters-eluting everything in its path there are organic compounds belonging to the so-called "persistent organic pollutants" (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzodioxins, polychlorinated dibenzofurans (PCDD and PCDF) and polychlorinated bi- and terphenyls (PCBs and PCTs) [13]. In periods when there is no flooding, soil is also exposed (although to a much lesser extent) persistent organic pollutants (including PAHs) as a result of dry deposition precipitation.

The group PAHs' include more than 200 compounds, however, for the monitoring purposes 16 were chosen that were characterized by particularly toxic (carcinogenic and mutagenic) properties. These compounds are characterized by the so-called chronic toxicity, which means that the dose is harmful in the case of prolonged exposure [14].

Not only the floodwaters but also dry deposition precipitation may bring significant quantities of metals and POPs [9, 14]. Also, organic fertilization with manure or slurry, compost, and especially sewage sludge constitutes a process of "enriching" the soil not only in organic substances necessary for its cultivation, but also redundant organic

substances such as polycyclic hydrocarbons [16–20]. Number of noted compounds of PAHs in soils accelerate anaerobic conditions (as a result of fermentation of organic matter in the soil) often occurring with high groundwater levels, particularly during flooding, when the waters cover the soil for a long period of time [21]. Allochtonous compounds of PAHs that are getting into the soil are absorbed mainly in the humus layer [22]. Organic matters present in amounts above 0.1 % are largely responsible for the sorption of pollutants [23]. However, the compounds of PAHs, despite a relatively low solubility in water due to the accompanying substances, may migrate along the direction of water flow into the profile and can then be collected by plants or got into the aquifers causing contamination, particularly strong in the case of light soils [22, 24]. Interaction of PAHs depends not only on the sensitivity of the body, but mainly on the type and concentration of the compound, and the coexistence of the other PAH compounds of the group. It has been shown that pyrene enhances the damaging effects benzo[a]pyrene. The group of the most carcinogenic properties include benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[b]fluoranthene [14].

The article focuses on the results of a study simulating flooding. The study also evaluated the rate of migration of PAHs in light soils that was subjected to a short process of flooding completely covering the area as a factor that may eliminate the soil from cultivating intended for direct consumption.

### Materials and methods

The experiment used soil samples (type: mud river) from arable layer, with grain size characteristic for loamy soils. Before the experiment, the soil was dried at room temperature and sieved through a 2 mm diameter mesh.

The ash was obtained from the incineration of oak biomass in an open small furnace, and was then incinerated at 600 °C for 2 hours for small of uncompleatly burned particles removal and then sieved through a sieve with a mesh diameter of 2mm. For experimental purposes, the amount of fertilization used is 5.52 Mg to ash/ha (GP), what was calculated on the base standard amount of mineral fertilizing 2Mg CaO / ha. The same soil without the ash (series G) was used as a reference sample. The test soil was placed in a glass cylinder with dimensions of  $3 \times 15$  cm (106 cm<sup>3</sup>). Then on the surface of the soil in the cylinder, some "flood sediment" was placed containing heavy metals in amount of 2.00 g/cylinder. The "flood sediment" was made by mixing in a 1:1:1 ratio (m/m) of sapropel sediment derived from the dam reservoir Turawskie Large Lake, of LRM1 certified reference material (Gdansk University of Technology, Poland) and a certified reference material LRM-CC013a (BAM, Berlin, Germany). For the simulation of fine-grain flood sediment, the sediment, before it was used, was thoroughly ground in an agate mill and sieved through a sieve with a mesh diameter of 0.5 mm. The cylinder's edges were secured with quartz wool. Cylinders were filled completely using the rainwater with capillary ascension method and incubated in the dark at a constant temperature of  $22 \pm 0.2$  °C for a period of 7 days. On 7th day after filling, the water was removed. Then, simulating the precipitation, cylinders with soil were washed with rain water in amount of 30mm/week, and the analysis of metals in the soil cores were made on days 7<sup>th</sup>, 14<sup>th</sup>, 28<sup>th</sup> and 42<sup>nd</sup> after filling the cylinders. After removing the soil from the core glass cylinder, it was separated for analysis into sections a, b, c and d corresponding to depths 0–3, 3–6, 6–9 and 9–12 cm profile, in order to capture the metal penetration into the deeper layers of soil.

However Regulation of Polish Ministers of Environment (9 September 2002) according to soil standards (Regulation MOE 165) recommend for determination only 9 compounds from PAHs group, in this work were collected data about 16 compounds specified on US-EPA list [25]. In investigated samples were determined also: reaction (pH), EC, organic matter content, TOC (with methods specified in Polish Standards). Heavy metals (Zn, Cu, Cr, Ni, Pb, Cd, Mn) were determined in averaged samples for each segment, by taking 4 independent samples from the tested core layer. In addition, the following parameters in the soils were determined: pH, electrolytic conductivity (EC), the content of organic matter and organic carbon (methodology according to Polish Standards). The content of calcium, sodium, potassium and lithium was ascertained in wet mineralizates by FES method using BWB-XP apparatus. The content of the other analysed metals (Zn, Cu, Cr, Ni, Pb, Cd, Mn) was determined by using a spectrophotometer Thermo AAS iCE 3500 after wet microwave assisted mineralization in aqua regia using MARS-X device. Polycyclic aromatic hydrocarbons analysis was carried out in a few steps. First of all fresh samples were dried at room temperature with anhydrous sodium sulphate (POCH) [26]. Extraction was carried out by a DCM-hexane (GC-grade) mixture in a ratio of 1:9 (v/v) in extraction device fexIKA $\otimes$  [15, 19, 22]. Before GC analysis, the extracts were purified by aluminium oxide (Aldrich) on glass columns [27]. Inspissated elutes were analysed by a GC-MS method (Shimadzu GC 17A with MS-OP5000) on capillary column VF5-ms 60 m; ID 0.25 mm and if 0.25 µm. The temperature of the chromatograph injector was 300 °C while the detector was 320 °C. The oven temperature program: 80 °C - 8 minutes, heating 10 °C/min to 270 °C, heating 2 °C/min to 300 °C. Detector current 1.2 to 1.4 kV In each sample 16 single compounds were determined which are recommended for monitoring by U.S. Environmental Protection Agency (US-EPA): naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenantrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (B[a]ant), chrysene (Chr), benzo[b]fluoranthene (B[b]flt), benzo[k]fluoranthene (B[k]flt), benzo[a]pyrene (B[a]p), dibenzo[a,h]anthracene (D[a,h]ant), indeno[1,2,3-c,d]pyrene (Ind[123]P), benzo[g,h,i]perylene (B[ghi]per). The flow of a carrier gas (He) was adjusted to 1 cm<sup>3</sup>/min. Certified PAHs standards (US-106N 2000  $\mu$ g · cm<sup>-3</sup> of each compound; Ultra Scientific USA) were used in order to determine calibration curve. Recovery levels for this procedure were low for naphthalene (57–66 %), and higher (73–92 %) for the rest individual PAHs. Recovery procedure was based on dry samples of PAHs reference materials: "ERM-CC013a" (BAM, Berlin, Germany) and "LRM soil 1" (University of Technology, Gdansk, Poland). The detection limits ranged between  $0.05-0.1 \mu g/kg d.m.$  for particular PAHs. The uncertainly of the results was calculated as standard deviation value. In order to single out the petrogenic compounds, the PAHs content: ANT/(ANT + PHE), BaA/(BaA + CHR), FLA/(FLA + PYR) in liquid and solid fuel combustion were calculated.

#### **Results and discussion**

The analysed soils, before they were poured, differed in terms of physic-chemical parameters (Table 1). The use of ash from biomass in an amount corresponding to liming in a dose 2 Mg CaO/ha resulted in increasing the acidity by 0.74 degree and conductivity of the soil by more than 80  $\mu$ S/cm.

Table 1

Parameter	Р	G	GP	Ν	Regulation MOE 165 [25]
Reaction [pH]	11.47(0.01)	6.62(0.01)	7.36(0.01)	7.05(0.01)	
$EC \; [\mu S \cdot cm^{-1}]$	12130 (26)	93.4(5.6)	176.8(4.0)	1378(7.8)	_
Organic matter [% d.m.]	0.63(0.09)	3.11(0.22)	3.28(0.02)	8.02(0.22)	_
TOC [% d.m.]	0.02(0.00)	1.01(0.06)	1.02(0.05)	3.27(0.11)	_
CaO [% d.m.]	34.37	0.039	0.049	0.667	_
Na <sub>2</sub> O [% d.m.]	0.198	0.004	0.006	0.113	_
K <sub>2</sub> O [% d.m.]	8.217	0.094	0.164	0.332	_
$Zn [mg \cdot kg^{-1} d.m.]$	506.8	59.51	55.59	919.0	300
Cu [mg $\cdot$ kg <sup>-1</sup> d.m.]	119.6	4.4	4.39	81.41	150
Pb [mg $\cdot$ kg <sup>-1</sup> d.m.]	21.23	13.99	15.07	70.79	100
$Cr [mg \cdot kg^{-1} d.m.]$	21.81	4.40	5.13	32.14	150
$Cd [mg \cdot kg^{-1} d.m.]$	2.27	< 0.2	< 0.2	17.07	4
Ni $[mg \cdot kg^{-1} d.m.]$	22.2	2.46	2.51	22.72	100
Mn [mg $\cdot$ kg <sup>-1</sup> d.m.]	4544	261.4	332.0	455.9	—

Characteristic of biomass ash (P) experimental soils (G, GP) and "flood sediment" (N) (n = 3)

- no regulation limit.

The use of ash from biomass also resulted in a slight increase in the content of heavy metals, except for manganese. Due to its significant content in the ash, over 27 % increase was noted in this element. The prepared slit from flooding was characterized by neutral reaction and relatively high conductivity. It contained more than 8 % organic matter, which is similar to that of the slit from rivers.

PAHs compounds were identified in the studied soil samples also before flooding. The addition of silt with PAHs above 40  $[mg \cdot kg^{-1} d.m.]$  (Table 2) washed with rainwater should become an important source of additional contamination of the soil profile. Larger amounts of PAHs, primarily due to the content of these compounds in the slit – their migration along with soil micro-particles and humus acid molecules, where PAHs are adsorbed, as well as due to the process of anaerobic decomposition of soil organic matter, and the organic matter permeating into the soil from silt. PAH fraction soluble in water is negligible and, usually do not exceed a few percent of the total content [28]. Decomposition of organic matter (and thus the decline in organic carbon) in the flooded soil is a natural phenomenon, which may increase the rate of transport of PAH [29]. Organic matter can slow the movement of these compounds as

a result of the sorption or even help to reduce the concentration of these contaminants, as a result of degradation by soil microflora [30]. Also composting process could reduce content of PAHs in soil or sewage sludge [31].

Table 2

Compound	G	GP	N	Regulation MOE 165 [25]
Naph	41.816	40.434	373.63	100
Acy	29.478	35.106	248.09	nl
Ace	36.353	40.434	342.74	nl
Flu	44.264	60.223	432.91	100
Phe	80.429	88.764	4705.2	100
Ant	149.65	156.50	1548.0	nl
Flt	130.25	180.67	6403.5	100
Pyr	129.69	150.79	4694.3	nl
B[a]ant	98.700	111.12	3185.5	100
Chr	156.43	180.57	5834.6	100
B[b]flt	109.34	116.73	2891.6	nl
B[k]flt	151.16	173.53	3531.4	100
B[a]p	76.003	86.957	2192.6	30
Ind[123]p	57.544	89.525	1030.6	nl
D[ah]ant	udl	udl	419.13	nl
B[g,h,i]per	5.180	9.038	2602.8	100
Σ ΡΑΗ	784.23	931.31	29262	1000
Σ 16 ΡΑΗ	1296.3	1520.4	40436	nl

PAH's content in experimental soils (G, GP) and "flood sediment" (N) [ $\mu$ g · kg<sup>-1</sup> d.m.]

udl - under detection limit; nl - no limit value.

The content of the tested 16 compounds from the group of PAHs before the start of the experiment was similar in both series of research (G and GP). Compound whose occurrence was not recorded in the soils was D[ah]ant (Table 2). However, in soil layer group b classified as agricultural land, some exceeding was recorded above the permissible concentrations in the surface layer (0–30 cm) in the case of Flt, B[a]ant, Chr, B[k]flt, and B[a]p. Indicator compound with proven carcinogenic and mutagenic properties is benzo(a)pyrene which permissible content in the soils of this group has been set at 30  $\mu$ g kg<sup>-1</sup> d.m. [25]. The calculated ratios of individual compounds in samples G, indicates anthropogenic character (derived mainly from the combustion of liquid and solid fuels) of determined PAHs.

Prepared for experimental purposes flood silt contained significant amounts of the analysed compounds (the amount of  $16WWA > 40 \text{ mg} \cdot \text{kg}^{-1} \text{ d.m.}$ ) and almost 30 times more than the permissible level specified regulations (Regulation MOE 165) and 20

times more than in soils from second-hand car marketplace [25, 32]. So high content of PAHs compounds could effect total toxicity effect for wide number of organisms [33].

Rainwater used in experiment (Table 3) was characterized by a basic reaction, a small electrolytic conductivity and relatively low content of organic matter.

Table 3

Parameter	Rainwater	Effluent G	Effluent GP
pН	8.97	7.25	7.97
EC [ $\mu$ S · cm <sup>-1</sup> ]	100.4	594	689
COD-Mn $[mgO_2 \cdot dm^{-3}]$	5.8	56.2	76.2

Characteristic of rainwater used for flooding experimental cylinders and effluent after 7-day of experiment

The effluents obtained from the cylinders after 7 days of incubation were characterized with near neutral reaction (G) and slightly alkaline (GP), increased electrolytic conductivity, and a high value of  $ChZT_{Mn}$ . A higher content of dissolved organic matter (DOM) in the GP series shows intense putrefaction in the cylinders with the addition of ash. This is probably the result of filling the pores of the soil with ash and intensifying degradation as a result of enrichment the solution in the macro- and micronutrients necessary for the proper development of the anaerobic flora. Washed organic matter contains absorbed compounds of PAHs, which with their low solubility in water allows them to migrate into the soil profile, and hence s hould cause higher concentrations of the test compounds than in the control group G [28].

Hydromorphic soils, even unpolluted, may contain higher amounts of PAHs than recorded in prepared for experimental purposes "slit", reaching even 200–249.6 mg  $\cdot$  kg<sup>-1</sup> in the layer of 0–5 cm [2, 4]. Exposure to periodic inundation by flood water, for example on terraces or flood polders, also increases the amount of PAHs in the soil on those areas in which the value was recorded above 24 mg  $\cdot$  kg<sup>-1</sup> dm for the amount of 19 compounds of this group [23]. The PAH content in the top layer of soil is largely dependent on land use. Urban soils, exposed to pollutants not only communication, but also industrial, contain 5–10 times more PAHs than agricultural soils. This is especially true of 5- and 6-ring compounds [1, 32]. However, pollution from the flood also plays a significant role in the context of the agricultural use of flooded areas. Level Ah soil (0–12 cm) oxbow of the Rhine contained more than 3.6 mg of the sum of 13 PAHs in kg  $\cdot$  d.m. [34].

In the experiment there was only a small migration of compounds of PAHs into the profiles of the soils (Fig. 1–15). An increase in concentration in all layers was observed only in the case of Flt and B[ghi]Per, with an average of 110 and 223 %. The nature of migration in both series (G and GP) was similar for the following: Ace, Flu, Ant, for which there were high correlation coefficients at 0.80–0.95 for all layers. In addition, strong correlations (0.77–0.95) were also recorded for B[a]P, Ind[123]P and B[ghi]Per, however, these relationships did not occur in all layers. We did not detect the expected significant increase of concentration of 16 PAHs in layers a and b as a result of the



Fig. 1. Naphtalene content changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods



Fig. 2. Acenaphtylene content  $[\mu g \cdot kg^{-1} d.m.]$  changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods



Fig. 3. Acenaphtene content  $[\mu g \cdot kg^{-1} d.m.]$  changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods



Fig. 4. Fluorene content  $[\mu g \cdot kg^{-1} \text{ d.m.}]$  changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods



Fig. 5. Phenanthrene content  $[\mu g \cdot kg^{-1} d.m.]$  changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods



Fig. 6. Anthracene content  $[\mu g \cdot kg^{-1} d.m.]$  changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods



Fig. 7. Fluoranthene content  $[\mu g \cdot kg^{-1} d.m.]$  changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods



Fig. 8. Pyrene content  $[\mu g \cdot kg^{-1} d.m.]$  changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods



Fig. 9. Benzo[a]anthracene content [μg · kg<sup>-1</sup> d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods



Fig. 10. Chrysene content [μg · kg<sup>-1</sup> d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods



Fig. 11. Benzo[b]fluoranthene content [ $\mu g \cdot kg^{-1}$  d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods



Fig. 12. Benzo[k]fluoranthene content [ $\mu g \cdot kg^{-1} d.m.$ ] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods



Fig. 13. Benzo[a]pyrene content [µg · kg<sup>-1</sup> d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods



Fig. 14. Indeno[1,2,3-cd]pyrene content [μg · kg<sup>-1</sup> d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods



Fig. 15. Benzo[g,h,i]perylene content [μg · kg<sup>-1</sup> d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

migration of silt microparticles by the profiles of the soils. The increase in acenaphthylene on day 7<sup>th</sup> of the experiment was only recorded for G series and naphthalene and acenaphthylene in a GP series. In the experiment there was observed increased concentrations (light) of 2-, and 3-ring compounds in all layers of the profiles. Moreover, in the GP series an increase of concentrations was noted for Flt, Pyr, Chr, B[b]flt, B[k]flt, B[a]P and Ind[123]P, primarily in the layer "c" on the 14<sup>th</sup> day.

Analysing the content of PAHs in all studied layers (a–d), a similar distribution of concentrations was observed only for the Ant of G series (corr. coef. 0.91–0.98) and for Acy, Flu, and Ant of GP series (corr. coef. 0.91–0.99).

Moreover, in the GP series, greater volatility of concentrations was observed in the different layers of the profile in relation to small variations recorded in a series of controls (G). In particular, this phenomenon clearly occurred at concentrations of 4- and 6-ring, PAHs that is from Flt to B[ghi]Per.

There was no clear positive correlation between the PAHs concentrations and heavy metals tested, what indicates a different mechanism of migration in the soil. Single correlations for, among others, nickel, zinc and lead with the compounds of PAHs appear to be random in nature. Other studies suggest a significant role of bacteria, which may contribute to changes in the mobility of bi-directional zinc and lead in the soil depending on the conditions [35]. Since the migration of PAH in a soluble form is small (the concentrations of few ng dm<sup>-3</sup> of four compounds), the movement of these compounds in the soil should be attributed mainly to the fraction adsorbed on the microparticles, while the metals migrate freely also in soluble forms [28].

A decrease was observed in concentrations of the individual compounds of the experiment after 42 days in comparison to the initial concentration (before pouring). This phenomenon was observed for both tested series. However, for the GP series the recorded concentrations of values were lower by 10.5–89 % compared to the final concentrations recorded for the G series.

Our simulation has not confirmed the increase in PAH concentration achieved in the model experiment in which distilled and sewage water were used to filling [36]. Following the release of water we investigated changes in the occurrence of PAHs in soil. In both cases, until 28th day of the experiment the PAH content increased by 28 and 38 % respectively for distilled and sewage water. After this time there was a decrease in the contents of the tested compounds. However, the behaviour of individual groups of compounds was varied. The strongest growth was recorded for 5- and 6-ring PAH. In the case of the "flood" simulated with distilled water, the final content of PAH (56<sup>th</sup> day) was less than 11-35 % compared to the start of the experiment. Probably the 7-day flooding by rainwater was too short to initiate the process of formation of PAHs or organic matter content in the soils was too low (3.11 and 3.28 %) for empirical confirmation of this phenomenon, which can occur with low intensity. However, in the case of the use of sewage water in the experiment by Oleszczuk et al, the final concentrations of the test compounds were higher than the initial one, which were from 11 to 130 %. This underlines the negative impact of soil contaminated by floodwaters due to providing substances that can increase the solubility and therefore bioavailability of PAHs [36].

The movement of PAHs along with the water penetrating the soil was tested in similar model experiments. The study was performed on mineral, organic and cultivated soil with organic carbon contents respectively 0.11, 16.3 and 10.1 %. The authors showed significant mobility of PAHs (fluorene, anthracene and pyrene) in mineral soil in which after 20 days of the experiment the tested compounds were recorded at a depth of 36 cm; whereas, in the case of cultivated and organic soil the tested compounds did not exceed the depth of 30 cm after 30 days the experiment. This has to do with the size of sorption complex (especially in the absence of anthropogenic contaminants such as ash or tar) and the permeability of the soils studied [37]. Experiment made here in, and the results obtained, despite the use of light, low in organic matter content soil, have not confirmed so significant motility of test compounds. In the studies the used ash from biomass caused an increase in the levels of certain compounds of PAHs in the layer c on day 14<sup>th</sup> of the experiment. This was mainly Phe, Flt, Pyr, and 5- and 6-ring PAHs. Then, however, the concentration of PAHs in this layer decreased and on day 42<sup>nd</sup> of the experiment the highest concentrations of these compounds were recorded in the layer "a" having direct contact with the slit.

## Conclusions

The use of prepared silt in a laboratory experiment did not bring the expected results. The expected significant increase of concentration of 16 PAHs in the layer "a" having direct contact with the slit did not occur. A significant increase in the concentrations of PAHs in the soils in the 42<sup>nd</sup> day of the experiment was observed only in the case of Flt and B[ghi]Per. In the case of acenaphthylene and phenanthrene and pyrene, chrysene, also noted a slight increase in their amount, but only in certain layers of soil cores analysed. The decrease in the sum of the 16 PAHs compounds studied in the 42<sup>nd</sup>-day experiment, with only periodic increase in the concentrations of individual compounds in the layer c suggests a small degree of transport of these compounds used in the experiment silt in which the content of the analysed compounds was high.

#### References

- Agarwal T, Khillare PS, Shridhar V, Ray S. Pattern, sources and toxic potential of PAHs in the agricultural soils of Delhi, India. J Hazard Mater. 2009;163:1033-1039. DOI:10.1016/j.jhazmat.2008.07.058.
- [2] Atanassova I, Brummer G. Polycyclic aromatic hydrocarbons of anthropogenic and biopedogenic origin in a colluviated hydromorphic soil of Western Europe, Geoderma. 2004;120:27-34. DOI: 10.1016/j.geoderma.2003.08.007.
- [3] Barbusiński K, Nocoń W. Zawartość związków metali ciężkich w osadach dennych Kłodnicy (Hazardous organic and trace element occurrence in bottom sediments of dam reservoirs). Environ Pollut Control. 2011;33;1:13-17.
- [4] Thiele S, Brummer GW. Bioformation of polycyclic aromatic hydrocarbons in soil under oxygen deficient conditions. Soil Biol Biochem. 2002;34:733-735.
- [5] Bojakowska I. Characteristic of polycyclic aromatic hydrocarbons and their occurrence in environment Bulletin of Polish Geological Institute. 2003;405:5-28.
- [6] Carlstrom CJ, Tuovinen OH. Mineralization of phenanthrene and fluoranthene in yardwaste compost. Environ Pollut. 2003;124:81-91.

- [7] Chen B, Xuan X, Zhu L, Wang JJ, Gao Y, Yang K, Shen X, Lou B. Distributions of polycyclic aromatic hydrocarbons in surface waters, sediments and soils of Hangzhou City, China. Water Research. 2004;38: 3558-3568.
- [8] Klanova J, Matykiewiczova N, Macka Z, Prosek P, Laska K, Klan P. Persistent organic pollutants in soils and sediments from James Ross Island, Antarctica. Environ Pollut. 2008;152:416-423. DOI: 10.1016/j.envpol.2007.06.026.
- [9] Wilcke W, Krauss M, Lilienfein J, Amelung W. Polycyclic aromatic hydrocarbons Storage in a typical cerrado of the Brazilian Savanna. J Environ Qual. 2004;33(3):946-955.
- [10] Włodarczyk-Makuła M, Janosz-Rajczyk M, Zakrzewska E, Karwowska B. Changes of PAHs contents in the sewage sludge and supernatants during anaerobic digestion process. Ecol Chem Eng. 2003;10(7):687-694.
- [11] Mouhri A, Motelay-Massei A, Massei N, Fournier M, Laignel B. Polycyclic aromatic hydrocarbon transport on the scale of a flood event on a rural watershed of Le Bebec, France. Chemosphere. 2008;73:443-450. DOI:10.1016/j.chemosphere.2008.05.046.
- [12] Magiera J. Rerafinacja olejów przepracowanych (Rerafination of used oils). Warszawa: Wyd Nauk--Techn;2006.
- [13] Witt G, Siegel H. The Consequences of the Oder Flood in 1997 on the Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in the Oder River Estuary. Mar Pollut Bull. 2000;40(12):1124-1131.
- [14] Gryglewicz G. Determination of polycyclic aromatic hydrocarbons in soil samples by gas chromatohraphy with mas spectrometry (GC-MS). Wrocław: Wrocław University of Technology, Faculty of Chemistry Chair of Polymer and Coal Materials; 2007 (non published materials).
- [15] Laskowski S, Trawczyńska A, Tołoczko W. Polycyclic aromatic Hydrocarbons (PAHs) in arable soils in proximity of communication tracts near Lodz City. Ecol Chem Eng. 2005;12(7):709-715.
- [16] Brandli RC, Bucheli TD, Kupper D, Furrer R, Stadelmann FX, Tarradellas J. Persistent organic pollutants in source-separated compost and its feedstock materials – a review for field study. J Environ Qual. 2005;34(3): 735-760. DOI: 10/2134/jeg2004.0333.
- [17] Mazur T, Mazur Z, Baran S, Oleszczuk P. Concentrations of polycyclic aromatic hydrocarbons (PAHs) in gray-brown podsolic soil as dependent on long-term fertilization. Ecol Chem Eng. 2006;13(9):947-952.
- [18] Oleszczuk P. Persistence of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge amended soil. Chemosphere. 2006;65:1616-1626. doi:10.1016/j.chemosphere.2006.03.007.
- [19] Oleszczuk P. Organic pollutants in sewage sludge-amended soil. Part II. Fate of contaminants in soils. Ecol Chem Eng. 2007;14(2):185-198.
- [20] Weber J, Karczewska A, Drozd J, Liczna M, Liczna S, Jamroz E, Kocowicz A. Agricultural and ecological aspects of a sandy soil as affected by the application of municipal solid waste composts. Soil Biol Biochem. 2007;39:1294-1302. DOI: 10.1016/j.soilbio.2006.12.005.
- [21] Włodarczyk-Makuła M, Janosz-Rajczyk M. Changes of PAHs concentration In sewage sludge modified by ZnCl<sub>2</sub>. Arch Environ Prot. 2004;32(3): 83-96.
- [22] Kluska M. Dynamics of soil sorption of polycyclic aromatic hydrocarbons in the vicinity of routes with intensive traffic. Arch Environ Prot. 2004;30(2):83-93.
- [23] Yang Y, Ligouis B, Pies C, Grathwohl P, Hofmann T. Occurrence of coal and coal-derived particle-bound polycyclic aromatic hydrocarbons (PAHs) in a river floodplain soil. Environ Pollut. 2008;151:121-129. DOI.org/10.1016/j.envpol.2007.02.020.
- [24] Ciesielczuk T, Kusza G, Poluszyńska J. Assessment of PAHs and the total content of organic master In landfill leachate and groundwater. Ecol Chem Eng A. 2006;13(11): 1225-1230.
- [25] Regulation of Ministry of Environment from 9 September 2002 according to soil and ground quality standards (J of Law 2002, 165 pos. 1359).
- [26] Ciesielczuk T, Rosik-Dulewska Cz, Nabzdyjak T. Distribution of aliphatic and polycyclic aromatic hydrocarbons in groundwaters in the airport fuel store area. Ecol Chem Eng A. 2006;13(4):531-538.
- [27] Wilcke W, Muller S, Kanchanakool N, Niamskul C, Zech W. Polycyclic aromatic hydrocarbons in hydromorphic soils of the tropical metropolis Bangkok. Geoderma. 1999;91:297-309.
- [28] Enell A, Fuhrman F, Lundin L, Warfvinge P, Thelin G. Polycyclic aromatic hydrocarbons in ash: Determination of total and leachable concentrations. Environ Pollut. 2008;152:285-292. DOI: 10.1016/j.envpol.2007.06.055.
- [29] Unger IM, Motavalli PP, Muzika RM. Changes in soil chemical properties with flooding: A field laboratory approach. Agric Ecosyst Environ. 2009;131:105-110. DOI: 10.1016/j.agee.2008.09.013.

- [30] Puglisi E, Cappa F, Fragoulis G, Trevisan M, Del Re AAM. Bioavailability and degradation of phenanthrene in compost amended soils. Chemosphere. 2007;67:548-556. DOI: 10.1016/j.chemosphere.2006.09.058.
- [31] Poluszyńska J. Biodegradtion von mehrkernigenaromatischen Kohlenwasserstoffen (MAK) im Kompostierungsprozess von kommunalen Klarschlammen. Scientific Works of Institute of Ceramics and Building Materials. 2012;10:395-407.
- [32] Szczepocka A, Prędecka A, Pawlak A. The influence of road infrastructure on the pollution levels by PAH and petroleum components on example of the car market in Slomczyn. Environmental Protection and Natural Resources. 2007;31(30):149-153.
- [33] Wolska L, Mędrzycka K. Assessing the ecotoxicity of the bottom sediments from the sea ports of Gdansk and Gdynia. Environ Pollut Control. 2009;31(1):49-52.
- [34] Gocht T, Moldenhauer KM, Puttmann W. Historical record of polycyclic aromatic hydrocarbons (PAH) and heavy metals in floodplain sediments from the Rhine River (Hessisches Ried, Germany). Appl Geochem. 2001;16:1707-1721.
- [35] Wu SC, Luo YM, Cheung KC, Wong MH. Influence of bacteria on Pb and Zn speciation, mobility and bioavailability in soil: A laboratory study. Environ Pollut. 2006;144:765-773. DOI.org/10.1016/j.envpol.2006.02.022.
- [36] Oleszczuk P, Baran S, Baranowska E, Pranagal J. Content of polycyclic aromatic hydrocarbons in long-term flooded soil – model research. Ecol Chem Eng S. 2007;14(1):109-116.
- [37] Czop M, Wandrasz JW. Procesy ruchu wielopierścieniowych węglowodorów aromatycznych w glebach. Environ Protect Natural Resour. 2007;31:144-148.

#### MIGRACJA WWA W WARSTWIE ORNEJ GLEB ZALANYCH WODAMI POWODZIOWYMI – DOŚWIADCZENIE MODELOWE

- <sup>1</sup> Katedra Ochrony Powierzchni Ziemi, Uniwersytet Opolski
  - <sup>2</sup> Instytut Podstaw Inżynierii Środowiska PAN, Zabrze
  - <sup>3</sup> Instytut Ceramiki i Materiałów Budowlanych, Opole

Abstrakt: Gleby okresowo lub stale podmokłe, a także gleby narażone na oddziaływanie wód powodziowych w znacznym stopniu narażone są na zanieczyszczenie związkami nieorganicznymi oraz organicznymi. Są to przede wszystkim te związki, które są nanoszone wraz z napływającą (silnie obciążoną) wodą powodziową, jak i autochtonicznymi wytwarzanymi w obrębie profilu glebowego, na drodze beztlenowych przemian materii organicznej. Związki z grupy WWA są sorbowane przez glebę z wód powodziowych oraz przemieszczają się w profilu glebowym, stanowiąc zagrożenie dla wód podziemnych. Ponadto po ustąpieniu zjawiska powodzi związki te mogą być pobierane przez rośliny uprawne. W pracy badano zanieczyszczenie gleb wielopierścieniowymi węglowodorami aromatycznymi (WWA) pochodzącymi z rozkładu materii organicznej oraz z nanosu powodziowego oraz ich migrację w warstwie ornej gleby.

Słowa kluczowe: powódź, WWA, gleby, migracja zanieczyszczeń