Polish Journal of Environmental Studies Vol. 14, No 4 (2005), 491-500

Original Research

Leaching of Individual PAHs in Soil Varies with the Amounts of Sewage Sludge Applied and Total Organic Carbon Content

P. Oleszczuk*, S. Baran

Institute of Soil Science and Environmental Management, Agriculture University, ul. Leszczyńskiego 7, 20-069 Lublin, Poland

Received: May 25, 2004
Accepted: December 10, 2004

Abstract

The aim of the work was the evaluation of the ability of individual PAHs from the US EPA list to migrate in relation to the sludge dose applied. On the basis of statistical analysis, an attempt was undertaken to evaluate the role of organic matter (total content of organic carbon) in the transportation of individual PAHs. Different doses of sewage sludge were introduced into the soil starting with a fertilizing dose (30 $t \cdot ha^{-1}$), through melioration doses (75, 150, 300 $t \cdot ha^{-1}$) to extreme doses (600 $t \cdot ha^{-1}$). A few days after the application of sewage sludge, the increase of PAHs was noted in the 20-40 cm soil horizon. The range of increase depended on the sewage sludge dose applied. The highest increase in PAH content was observed in soil with a sludge dose of 300 $t \cdot ha^{-1}$. However, after an 18-month period of study, the relationships observed before changed and the highest increase of individual PAHs in the 20-40 cm soil horizon relative to the control was noted in the case of the highest sludge dose.

Keywords: sewage sludge, polycyclic aromatic hydrocarbons, organic contaminants, soil fertilization, PAH leaching

Introduction

Due to the origins of sewage treated, sludge can contain pollutants different both in quantity and quality. Polycyclic aromatic hydrocarbons are pollutants that frequently occur in sewage sludge and their content can vary over very broad ranges [1-4]. The presence of polycyclic aromatic hydrocarbons in the environment is related to [5, 6] human activities (emission from industrial plants and power plants, transportation, introduction of sewage sludge and compost used as fertilizers, road runoff, sewage drains, vehicle and machinery fuel and grease, substances introduced during pollution break-down with crude oil derivatives) and natural processes (vegetation fires, volcanic activity) or biogenic orgins (surface waxes of leaves, plant oils, cuticles of insects).

Most PAHs are characterized by highly toxic, mutagenic and carcinogenic properties; and due to their high durability in the environment, they belong to the group of persistent organic pollutants (POPs).

Despite the fact that PAHs show a strong affinity to organic matter, it has often been proved in the literature [7-10] that they can be transferred deeper into the soil profile, which is related to the risk of groundwater pollution.

The aim of the present work was to evaluate the migration of individual PAHs from the US EPA list in relation to the sludge dose applied. On the basis of statistical analysis, an attempt was undertaken to determine the role

* Corresponding author; e-mail: patol@consus.ar.lublin.pl or eco@poczta.fm

of organic matter (on the basis of total carbon content) in the transportation of individual PAHs.

Materials and Methods

Plot Experiment

The study block consisted of six plots, 15 m^2 each, founded on light soils (containing — 86% sand, 7% silt and 7% clay) originating from weakly clayed sand. The soil into which sewage sludge was introduced were characterized by pH — 6.0, cation exchange capacity — 13.4 $mmol \cdot kg^{-1}$, total of exchangeable bases — 59.9 $mmol \cdot kg^{-1}$, the degree of base saturation — 22%), and small content of organic carbon and total nitrogen — 10.7 and 1.4 $g \cdot kg^{-1}$, respectively. Before, as well as during the experiment, control soil and sewage sludge-amended soil were subject to wet and dry deposition. More detailed description of effect of atmospheric deposition on PAH content in control soil, as well as possible sources of pollution, can be found in other papers [11]. Analysis of data (data not presented) showed that the process of atmospheric deposition does not play a significant role in the fate of PAHs in sewage sludge-amended soil.

Plots were located according to increasing doses of sludge as follows: sewage sludge 30 $t \cdot ha^{-1}$ (1%); 75 $t \cdot ha^{-1}$ (2.5%); 150 $t \cdot ha^{-1}$ (5%); 300 $t \cdot ha^{-1}$ (10%); 600 $t \cdot ha^{-1}$ (20%). Control soil was "treated" the same as sludge-amended soil, the only difference being that no sewage sludge was introduced to it. In both control and sludge-amended soil perennial plant — willow (*Salix vinimalis*) was cultivated.

Soil-like, fermented sewage sludge from a mechanical-biological sewage treatment plant originating from communal (70%) and industrial (30%) waste was used for the present experiment. The amount of sludge applied was established taking into account fertilizing (30 $t \cdot ha^{-1}$), melioration (75-300 $t \cdot ha^{-1}$), and extreme doses (600 $t \cdot ha^{-1}$). The choice of extreme doses was aimed at establishing the degree at which soil becomes polluted with PAHs, and what the background is upon which the durability of these compounds is founded.

Sludge doses were calculated taking into consideration the sludge's dry mass and the density of the solid soil phase. It was mixed with a surface soil horizon up to a depth of 20 cm. The sewage sludge applied in the study was characterized by pH — 6.0, cation exchange capacity — 500.4 $mmol \cdot kg^{-1}$, total of exchangeable bases — 547.7 $mmol \cdot kg^{-1}$, degree of the base saturation — 99%), total content of organic carbon and total nitrogen — 210.0 and 17.8 $g \cdot kg^{-1}$, respectively. PAH concentration in sewage sludge used in the experiment was 5712 $\mu g \cdot kg^{-1}$. Detailed characteristics of sewage sludge used in the experiment and the soil into which it was introduced can be found in another work [12]. In other paper [13], details concerning possibilities of forecasting the content of individual PAHs in the soil, on the basis of their content in sewage sludge, were described.

Sample Collection and Preparation

Surface (0-20 cm) and subsurface (20-40 cm) soil and sewage sludge-amended samples were collected (after a period of 2 days, 6 and 18 months after sewage sludge application) with a (5 cm i. d. x 60 cm) stainless steel corer. Six independent samples (replicates) were taken from each plot, sliced into two parts (0-20 cm and 20-40 cm) and each part from a particular plot was mixed to obtain a representative sample. The cores were placed into zip-lock bags. Samples were transported to the laboratory, air-dried in air-conditioned storage rooms (20-25°C) for 2 d (in darkness), manually crushed and sieved prior to chemical analyses. Half of each sample for PAH determination was crushed and passed through a 2-mm sieve. However, the other half each sample for total organic carbon analysis (TOC) was passed through a 1-mm sieve.

Analysis of PAHs

PAH was determined using the method of HPLC with UV detection (254 nm) after optimisation of the analytic process with respect to the amount and type of solvent used and extraction time, by means of ultrasonic method [14] and optimization of the extract purification process by the solid phase extraction method (SPE, C18 Octadecyl columns, JT Baker-Mallinckrodt, Germany) [15].

A Spherisorb-PAH (250 x 4.6 mm I. D., 5 µm; Schambeck SFD GmbH, Germany) was used for PAH separation. The mobile phase (acetonitrile: water, 82: 18, v/v) flow was set to 1 mL min^{-1}. Detection was carried out at 254 nm. The column was installed in a thermostated oven at 31°C (LCO 101, ECOM, Czech Republic). All reported concentration values of PAHs are expressed on a dry-wt basis of soil (determined by drying the soils for 24 h at 105°C) and are the average of triplicate extraction.

Recoveries for the total procedures (sample preparation, extraction and SPE) ranged between 81-90% (in soil and sewage sludge-amended soil) and 72-83% (in sewage sludge) for individual PAHs. Only cases of naphthalene recoveries were in the range 50-60% (in all samples). Precision expressed as relative standard deviation (RSD) was below 21%. The data were not adjusted for recoveries.

Total Organic Carbon Content

Air-dry soil samples were mixed and sieved using a 1 mm sieve (according to the Polish Soil Science Society) to separate gravel (particles sizes >1 mm) and non-soil components. Total organic carbon (TOC) content was determined by Tiurin's method as modified by Simakow [16]. Fig. 1 presents total organic matter contents (TOC) in soil and sewage sludge-amended soils.

Data Analysis

Statistically significant differences between the results were evaluated on the basis of standard deviation determinations and analysis of variance method (ANOVA, 95% confidence intervals test). Pearson correlation coefficient was calculated. Significance was set at $P \leq 0.05$.

Results and Discussion

PAH Content in Control Soil

Table 1 presents changes in PAH content in control soil. A clear difference in relation to the type of PAH and also the experimental variant was found while evaluating the content of individual PAHs after 6 and 18 months from the beginning of the experiment.

After 18 months from the beginning of the experiment, in the control soil (a 0-20 cm soil horizon), a decrease was found only in the case of naphthalene, acenaphtene and dibenz [*ah*] anthracene. In the case of the remaining compounds, an increase was observed; it was highest for anthracene (171%), followed by benzo[*ghi*]perylene (170%), chryzene (95%) and benzo[*k*]fluoranthene (86%) (Table 1). The increase was most probably related to the atmos-

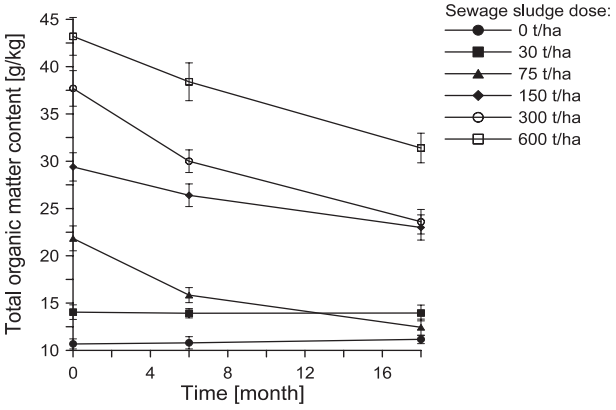

Fig. 1. Changes of total organic carbon content (TOC) in control soil (0 t/ha) and sewage sludge-amended soils (30-600 $t \cdot ha^{-1}$). Error bars represent standard deviation (SD, n=3).

Table 1. The content of individual PAHs in control soils 2 days, 6 and 18 months after beginning the experiment.

PAHs	Concentration of PAHs [$\mu g \cdot kg^{-1}$]					
	0-20 cm			20-40 cm		
	2 days	6 months	18 months	2 days	6 months	18 months
Na	3.0 (9)	2.7 (10)	2.5 (12)	1.7 (11)	1.8 (16)	1.7 (13)
Ace	13.0 (11)	14.0 (9)	14.9 (14)	13.3 (12)	12.6 (15)	12.2 (10)
Ac	10.6 (17)	10.1 (15)	10.2 (12)	10.9 (10)	10.4 (11)	10.0 (9)
Fl	3.6 (6)	3.5 (7)	4.7 (8)	2.5 (13)	3.3 (15)	2.4 (13)
Phen	0.8 (9)	0.9 (11)	1.2 (7)	0.7 (8)	0.9 (12)	0.9 (10)
Ant	0.1 (9)	0.1 (14)	0.3 (11)	0.0	0.2 (13)	0.2 (13)
Fln	2.4 (11)	2.2 (8)	3.6 (10)	1.1 (10)	2.9 (8)	2.0 (11)
Pyr	1.8 (8)	2.2 (7)	3.1 (9)	2.2 (13)	2.4 (10)	1.4 (9)
BaA	1.4 (4)	1.5 (6)	1.8 (8)	1.4 (9)	1.7 (12)	1.2 (13)
Ch	1.2 (14)	1.8 (11)	2.3 (7)	1.3 (9)	1.7 (12)	1.1 (13)
BbF	3.6 (21)	2.3 (14)	3.0 (16)	2.0 (11)	0.8 (11)	1.5 (14)
BkF	1.2 (18)	1.5 (17)	2.2 (13)	1.4 (7)	1.2 (9)	0.8 (10)
BaP	1.7 (15)	2.2 (15)	2.7 (11)	1.8 (12)	2.1 (9)	1.3 (9)
DahA	2.2 (6)	1.2 (7)	1.8 (6)	0.0	0.0	0.0
BghiP	0.7 (10)	0.8 (9)	1.9 (10)	0.4 (10)	1.0 (11)	1.5 (9)
IP	2.3 (11)	1.6 (9)	3.6 (9)	2.4 (13)	2.6 (10)	2.3 (8)
Σ PAHs	49.6 (11)	48.6 (11)	59.8 (10)	43.1 (11)	45.6 (11)	40.4 (12)

Na — Naphthalene, Ace — Acenaphthylene, Ac — Acenaphtene, Fl — Fluorene, Phen -Phenanthrene, Ant — Anthracene, Fln — Fluoranthene, Pyr — Pyrene, BaA — Benz [a] anthracene, Ch — Chrysene, BbF — Benzo [b] fluoranthene, BkF — Benzo [k] fluoranthene, BaP — Benzo [a] pyrene, DahA — Dibenz [a, h] anthracene, BghiP — Benzo [ghi] perylene, IP — Indeno [1,2,3-cd] pyrene; relative standard deviation (RSD, %) (n = 3 extractions) is presented in parentheses.

pheric deposition which played the main role in the distribution of PAH in the area studied. On the basis of the ratios calculated between individual PAH contents and also on the basis of the occurrence of the individual compounds of this group, it was found that the most probable source of PAHs were processes related to coal combustion (data not present). In the 20-40 cm soil horizon, the large increase was noted only in the case of anthracene (over 7-times), benzo[*ghi*]perylene (3-times), fluoranthene (86%) and phenanthrene (25%) (Table 1), which was undoubtedly related to the increased content of these compounds in the surface soil horizon (Table 1). In the case of the remaining PAHs, a systematic statisically significant decrease was observed in the case of acenaphtene only.

Only in the case of acenaphthylene and benzo[b]fluoranthene, were statistically significant ($P \leq 0.05$) negative relations found, while evaluating the relation in changes in the individual PAHs in the 20-40 cm soil horizon (Table 1) and their content in the 0-20 cm soil horizon (Table 1). For the remaining PAHs, these changes were not significant.

The Influence of Sewage Sludge on PAH Content

The introduction of sewage sludge into the soil resulted in an increased PAH content in the 20-40 cm soil horizon in those plots with a sludge dose of 75-600 t·ha^{-1} after the first two days. Data shows (Table 3, Fig. 2) that two days from the introduction of sludge a decrease in the content of naphthalene, acenaphthylene, acenaphtene, pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and indeno[1,2,3-cd]pyrene was observed only in the lowest dose (30 t·ha^{-1}). In the case of the remaining doses, a stable (systematic) increase of all individual PAH content was observed up to a sludge dose of 300 t·ha^{-1} (Fig. 2). In the experimental variant with the highest sludge dose, an increase in PAH content in relation to the control plot was observed; however, it was lower than in the plot with the dose of 300 t·ha^{-1}. This was reflected at a depth of 0-20 cm where the differences in PAH content between sludge doses of 300 and 600 t·ha^{-1} were very small (Table 2). The introduction of sewage sludge increases the amount of organic matter in the soil (first of all in the 0-20 cm soil horizon) (Fig. 2) which plays the role of a strong sorbent in relation to organic pollutants and regulates significantly the leaching of these compounds deeper into the soil profile. However, as can be seen on the basis of the studies carried out, the strength and range of influence of the organic matter in relation to PAHs is clearly dependent on the sewage sludge dose. In the case of experimental variants with 75-300 t·ha^{-1} sewage sludge contribution, despite the "sorption barrier" created by the organic matter, a gradual increase in PAH content in the 20-40 cm soil horizon with consecutive sewage sludge doses (Fig. 2) was observed. At a sludge dose of 600 t·ha^{-1}, the sorption abilities of organic matter in relation to PAHs are strong enough to clearly limit the PAHs leaching the surface horizon of the soil fertilized with sewage sludge. Soil with a sewage sludge content at a dose of 20% (and

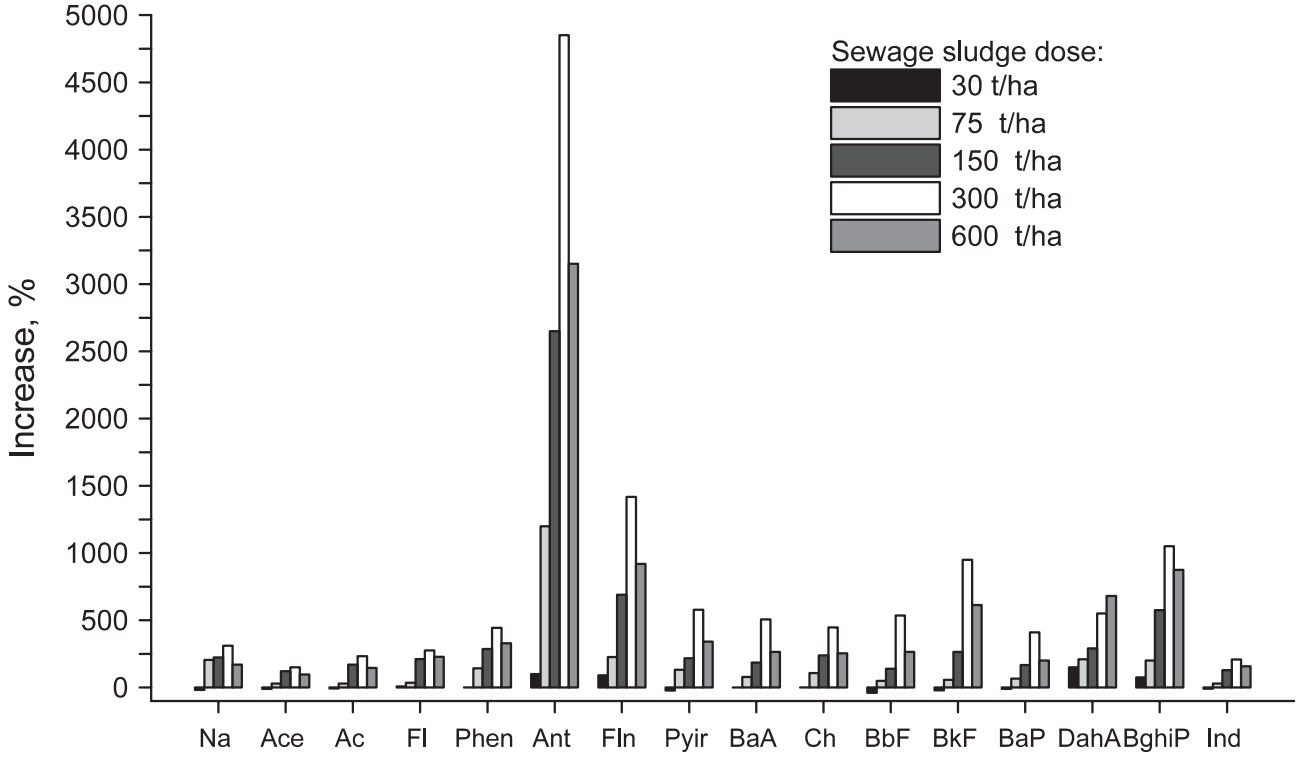

Fig. 2. Increase of PAH content in sewage sludge-amended soil in relation to control plot (after two days from sewage sludge introduction, horizon 20-40 cm).

Table 2. The content of individual PAHs in sewage sludge-amended soil (horizon 0-20 cm).

PAHs	Concentration of PAHs [µg•kg^{-1}]														
	30 t ha^{-1}			75 t ha^{-1}			150 t ha^{-1}			300 t ha^{-1}			600 t ha^{-1}		
	days	months		days	months		days	months		days	months		days	months	
	2	6	12	2	6	12	2	6	12	2	6	12	2	6	12
Na	5.5 (15)	8.1 (6)	3.2 (11)	18.5 (12)	14.0 (8)	13.1 (9)	40.1 (16)	11.8 (9)	10.5 (6)	87.8 (13)	15.5 (9)	13.7 (8)	95.0 (13)	36.4 (9)	41.6 (9)
Ace	16.0 (17)	21.7 (11)	16.9 (8)	41.1 (15)	24.5 (6)	33.3 (6)	59.4 (12)	29.2 (11)	53.2 (7)	115.0 (17)	39.5 (8)	71.1 (8)	143.8 (15)	107.3 (8)	128.4 (9)
Ac	11.2 (9)	15.3 (4)	10.9 (9)	19.0 (12)	16.8 (9)	16.9 (7)	46.0 (15)	21.8 (13)	24.0 (9)	96.0 (13)	18.1 (7)	32.9 (6)	96.0 (13)	45.8 (6)	64.0 (8)
Fl	1.1 (11)	6.9 (7)	5.5 (4)	2.6 (8)	8.6 (11)	7.7 (11)	14.9 (9)	6.9 (15)	5.6 (14)	40.6 (9)	3.2 (11)	7.9 (11)	21.5 (10)	9.4 (13)	15.7 (6)
Phen	1.9 (9)	3.0 (8)	1.5 (6)	5.1 (11)	4.2 (14)	4.1 (16)	16.1 (12)	3.6 (7)	7.5 (11)	32.3 (8)	7.8 (13)	11.3 (9)	31.5 (11)	12.4 (11)	19.3 (6)
Ant	0.2 (7)	0.9 (11)	0.2 (7)	1.1 (11)	1.0 (6)	0.9 (12)	4.6 (13)	1.6 (9)	1.9 (7)	14.4 (10)	2.9 (9)	3.0 (14)	11.9 (10)	4.2 (16)	5.2 (12)
Fln	5.6 (19)	3.6 (9)	4.8 (9)	21.0 (13)	5.7 (15)	14.8 (7)	50.6 (18)	13.5 (9)	28.6 (8)	40.2 (12)	24.7 (9)	38.1 (5)	107.9 (14)	46.7 (6)	66.6 (7)
Pyr	3.3 (16)	8.0 (9)	4.8 (12)	2.5 (12)	13.6 (8)	11.3 (9)	41.1 (9)	9.2 (11)	25.4 (9)	109.6 (8)	20.8 (7)	37.9 (5)	111.3 (7)	46.9 (6)	75.0 (9)
B*a*A	5.0 (6)	4.5 (12)	2.3 (11)	6.7 (9)	6.9 (4)	5.0 (8)	20.3 (10)	5.1 (8)	10.4 (5)	65.8 (7)	10.3 (6)	14.4 (8)	62.2 (8)	21.4 (8)	24.0 (5)
Ch	1.1 (9)	4.2 (8)	2.5 (8)	10.2 (10)	6.1 (15)	6.2 (5)	14.4 (13)	6.5 (8)	10.8 (5)	34.5 (15)	14.4 (4)	16.5 (6)	47.2 (11)	23.8 (8)	26.4 (5)
B*b*F	4.4 (15)	5.3 (17)	3.2 (6)	10.2 (17)	7.2 (6)	6.5 (4)	58.1 (17)	21.4 (11)	11.6 (7)	62.1 (15)	14.0 (4)	17.8 (9)	69.6 (19)	25.6 (6)	30.9 (7)
B*k*F	2.8 (12)	2.2 (6)	2.2 (7)	5.2 (14)	7.1 (6)	4.2 (7)	7.9 (15)	4.9 (9)	6.7 (8)	23.6 (17)	8.0 (6)	10.2 (9)	30.2 (16)	15.2 (7)	17.2 (5)
B*a*P	4.8 (16)	4.9 (11)	3.3 (7)	11.1 (15)	7.1 (9)	6.8 (9)	17.5 (17)	9.0 (10)	12.9 (9)	53.7 (13)	15.0 (7)	18.8 (7)	45. 9 (15)	24.7 (9)	35.7 (8)
D*ah*A	3. 9 (9)	2.3 (12)	2.4 (1)1	6.3 (8)	2.4 (8)	5.0 (6)	13.5 (6)	26.0 (7)	6.9 (11)	44.1 (9)	11.7 (5)	14.2 (4)	63.6 (8)	24.3 (9)	27.9 (9)
B*ghi*P	2.7 (8)	1.9 (7)	2.6 (9)	8.4 (9)	4.4 (7)	5.1 (6)	10.9 (8)	5.6 (8)	7.5 (16)	28.4 (9)	11.2 (8)	17.2 (8)	31.2 (10)	18.7 (5)	27.3 (4)
IP	4.3 (7)	1.6 (9)	3.4 (6)	7.9 (12)	2.2 (9)	5.7 (7)	13.9 (10)	9.1 (8)	9.1 (11)	34.2 (10)	10.8 (9)	13.0 (7)	34.0 (8)	20.1 (5)	26.9 (7)
Σ 16 PAHs	73.8 (12)	94.3 (9)	69.8 (8)	176.9 (12)	131.8 (9)	146.6 (8)	429.3 (13)	185.2 (10)	232.6 (9)	882.3 (12)	227.9 (8)	338.0 (8)	1002.8 (12)	482.9 (8)	632.1 (7)

Description of individual PAHs in Table 1.

Table 3. The content of individual PAHs in sewage sludge-amended soil (horizon 20-40 cm).

PAHs	Concentration of PAHs [μg·kg^{-1}]														
	30 t ha^{-1}			75 t ha^{-1}			150 t ha^{-1}			300 t ha^{-1}			600 t ha^{-1}		
	days	months		days	months		days	months		days	months		days	months	
	2	6	12	2	6	12	2	6	12	2	6	12	2	6	12
Na	1.4 (13)	3.1 (11)	5.5 (9)	5.2 (11)	0.9±(8)	2.1 (14)	5.5 (15)	6.5 (12)	7.9 (15)	7.0 (13)	6.0 (16)	6.2 (15)	4.6 (15)	2.8 (14)	1.5 (11)
Ace	12.0 (17)	16.7 (7)	19.4 (9)	17.2 (11)	23.4 (11)	13.9 (17)	29.4 (19)	34.7 (20)	33.1 (17)	33.4 (18)	26.9 (9)	32.4 (8)	26.1 (15)	20.7 (16)	39.5 (9)
Ac	10.1 (11)	16.0 (9)	16.5 (7)	14.2 (12)	21.2 (14)	13.3 (20)	29.5 (21)	33.9 (15)	28.4 (14)	36.2 (17)	29.1 (8)	33.9 (9)	26.8 (19)	19.9 (25)	37.2 (9)
Fl	2.7 (8)	4.0 (5)	5.8 (5)	3.4 (9)	6.0 (13)	2.6 (14)	7.8 (15)	7.4 (9)	8.9 (10)	9.4 (12)	7.0 (11)	9.1 (13)	8.2 (10)	4.9 (13)	13.8 (8)
Phen	0.7 (10)	1.5 (8)	2.1 (11)	1.7 (7)	2.2 (9)	1.5 (10)	2.7 (8)	3.7 (10)	3.6 (10)	3.8 (9)	2.7 (10)	3.7 (12)	3.0 (7)	1.6 (8)	4.0 (11)
Ant	0.04 (9)	0.3 (14)	0.5 (9)	0.3 (13)	0.6 (8)	0.3 (8)	0.55 (9)	0.8 (9)	0.7 (8)	1.0 (8)	0.6 (9)	0.7 (10)	0.65 (9)	0.3 (13)	1.3 (12)
Fln	2.1 (9)	5.2 (11)	7.9 (8)	3.6 (17)	8.1 (16)	5.3 (16)	8.7 (13)	12.3 (15)	13.5 (13)	16.7 (11)	10.0 (9)	11.6 (9)	11.2 (5)	5.6 (7)	17.8 (9)
Pyr	1.7 (13)	4.3 (7)	6.6 (4)	5.1 (9)	7.4 (11)	4.4 (11)	7.0 (13)	10.4 (11)	11.0 (12)	14.9 (14)	8.9 (12)	8.0 (10)	9.7 (10)	5.1 (9)	16.4 (8)
B*a*A	1.4 (11)	2.5 (9)	3.4 (4)	2.5 (8)	4.5 (10)	2.4 (9)	4.0 (11)	6.0 (11)	6.4 (8)	8.5 (10)	5.1 (11)	5.4 (8)	5.1 (18)	3.3 (13)	9.4 (14)
Ch	1.3 (10)	2.4 (12)	3.3 (9)	2.7 (8)	3.3 (10)	2.4 (8)	4.4 (8)	5.4 (10)	5.7 (8)	7.1 (6)	4.0 (8)	5.7 (10)	4.6 (9)	3.0 (11)	7.1 (12)
B*b*F	1.2 (14)	0.8 (8)	0.8 (7)	3.0 (13)	0.8 (15)	0.8 (16)	4.8 (7)	1.6 (13)	1.6 (12)	12.7 (9)	1.3 (10)	1.3 (9)	7.3 (10)	1.3 (13)	1.3 (9)
B*k*F	1.1 (14)	1.0 (10)	2.1 (11)	2.2 (16)	3.4 (14)	1.6 (12)	5.1 (7)	1.7 (15)	4.1 (16)	14.7 (15)	2.3 (11)	3.5 (10)	10.0 (16)	2.1 (14)	2.7 (7)
B*a*P	1.6 (15)	2.7 (4)	4.5 (8)	3.0 (18)	5.8 (13)	3.0 (11)	4.8 (13)	6.0 (10)	9.3 (12)	9.2 (15)	4.7 (14)	7.7 (13)	5.4 (12)	3.3 (10)	0.0
D*ah*A	1.5 (8)	1.5 (9)	1.5 (9)	2.1 (4)	2.0 (7)	2.0 (6)	2.9 (6)	2.8 (7)	2.8 (9)	5.5 (3)	5.4 (6)	5.4 (5)	6.8 (8)	6.8 (9)	6.8 (11)
B*ghi*P	0.7 (9)	2.0 (7)	2.3 (10)	1.2 (10)	3.5 (9)	1.5 (7)	2.7 (9)	3.9 (9)	4.8 (8)	4.6 (8)	3.4 (7)	4.7 (6)	3.9 (8)	2.3 (7)	5.9 (9)
IP	2.2 (8)	3.3 (6)	2.5 (6)	3.1 (11)	4.4 (8)	2.1 (6)	5.5 (10)	6.8 (11)	4.1 (6)	7.4 (6)	5.8 (7)	7.2 (6)	6.2 (7)	4.4 (7)	7.9 (8)
Σ 16 PAHs	41.7 (11)	67.3 (9)	84.7 (8)	70.5 (11)	97.5 (11)	59.2 (12)	125.4 (12)	143.9 (12)	145.9 (11)	192.1 (11)	123.2 (10)	146.5 (10)	139.6 (11)	87.4 (12)	172.6 (10)

Description of individual PAHs in Table 1.

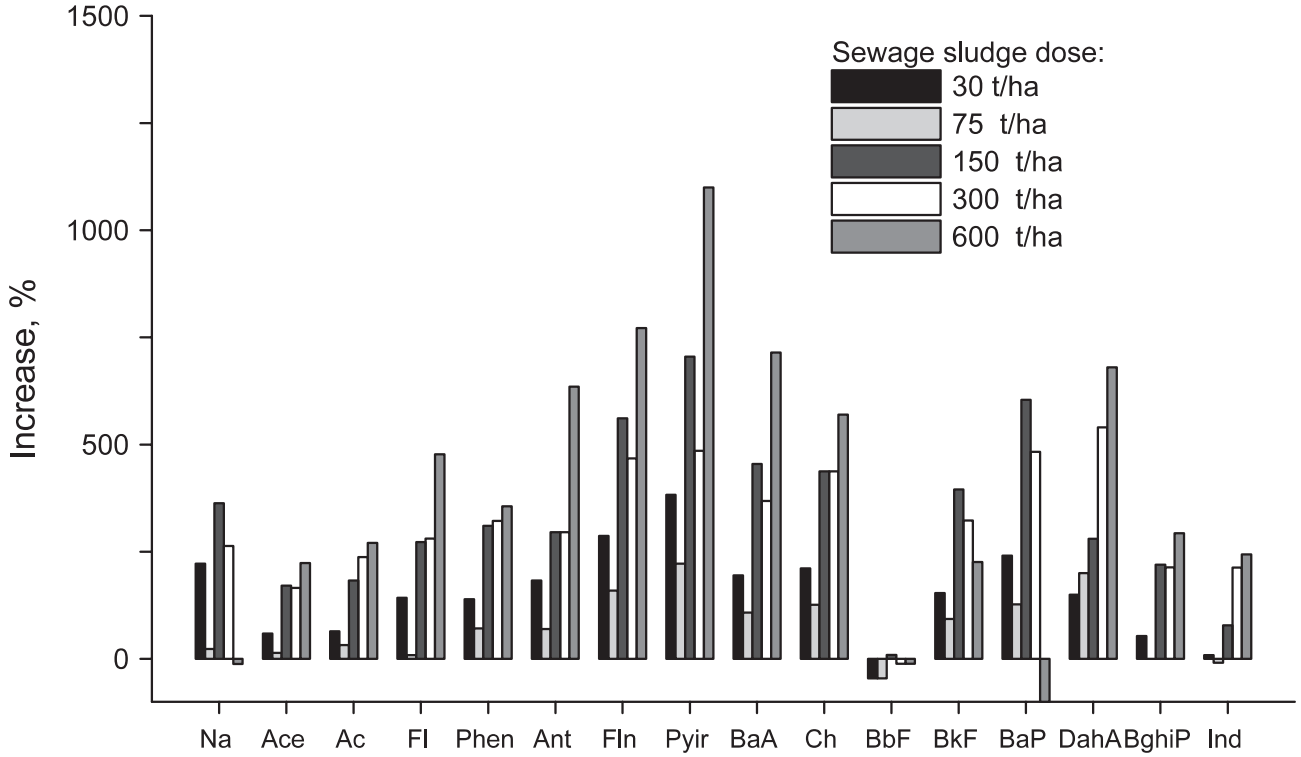

Fig. 3. Increase of PAH content in sewage sludge-amended soil in relation to control plot (18 months after from sewage sludge introduction, horizon 20-40 cm).

hence with a higher value of organic matter content) can show higher sorption abilities in relation to PAH than soil with a 1-10% sludge addition. Hence, it can be gathered that sorption processes at an increased amount of organic matter (soil with sewage sludge in dose 600 t/ha (20%)) are more intense and clearer than in soil fertilized by sewage sludge in lowest doses. Moreover, with an increase in sewage sludge mass added, there is an increase in the amount of organic matter of anthropogenic origin (dust, ash, and soot) [17], which exerts a stronger influence on the PAH than the influence exerted by natural matter. This effect is due to the "highly" aromatic character of this type of matter and its considerable specific surface area compared to natural organic matter [17].

Analysis of the changes in the content of individual PAHs in the 20-40 cm soil horizon in relation to their content in the 0-20 cm soil horizon (within 18 months), showed statistically significant relations only in the case of a few PAHs. Leaching of the individual PAHs deeper into the soil profile is undoubtedly related to their content in the 0-20 cm soil profile. However, on the basis of the calculations obtained, it can be assumed that the transportation process is specific and depends on several factors, including the properties of the PAHs.

The lack of the above relation in the remaining plots (e. g. 150 and 600 $t \cdot ha^{-1}$) could be evidence of the higher actual content of pollutants (e. g. strongly adsorbed ones) in the 0-20 cm soil horizon which are released secondarily. This is especially dangerous as it shows that repeated soil pollution (and pollutant uptake by plants) or pollutant migration deeper into the soil profile is possible. Many authors [18-23] have pointed to the possibility of the slow desorption of previously sequestrated organic pollutants (including PAHs).

Hence, it can be assumed that as a result of organic matter mineralization, release-desorption of PAHs in the 0-20 cm soil horizon takes place. Some migrate deeper into the soil profile while the remaining released PAH fraction continues to remain in the 0-20 cm soil horizon. Besides the changes in organic matter, surfactants commonly present in sewage sludge [24, 25] can influence the process of PAH desorption [26, 27] from the soil matrix alongside the changes in the organic matter. White et al. [22] described the possibilities of the displacement of phenantrene previously sequestrated as a result of "fresh" soil pollution with other PAHs (i. e. pyrene).

In the case of soil with a sewage sludge dose of 30 $t \cdot ha^{-1}$, a gradual increase in the content of all PAHs in the 20-40 horizon was observed. This may indicate a certain "weakening" of the sorption properties of organic matter in relation to PAHs in the 0-20 cm soil horizon. A similar relation was observed in the case of most PAHs in the soil in the experimental variants with a sludge dose of 150 and 600 $t \cdot ha^{-1}$. In the case of the sludge dose of 75 and 300 $t \cdot ha^{-1}$, after 18 months of the experiment, a decrease in their content in the 20-40 cm soil horizon was finally observed. The results obtained are illustrated by the data presented in Figures 2 and 3. Even though on the first date of sample collection (Fig. 2) the highest increase in the content of individual PAHs — in the 20-40 cm soil horizon as compared to the

control soil — was noted in the case of the sludge dose of 300 t·ha^{-1}, in the final stage of this experiment, the variant with the sludge dose of 600 t·ha^{-1} (except for naphthalene, benzo[b]fluoranthene and benzo[a]pyrene) clearly predominated. This confirms the hypothesis presented earlier that the sorption properties of soils fertilized with sludge at a dose of 600 t·ha^{-1} were weakened with time in relation to PAHs and hence transportation of individual PAHs deeper into the soil profile became possible.

Data quoted in literature [7, 28-31] indicates that PAH transportation deeper into the soil profile is possible. The clear influence of surfactants [29, 30, 35] and dissolved organic carbon (DOC) [33, 34] on PAH desorption has been evidenced. Moreover, soil colloids [32], some microorganisms [36], and also soil invertebrates (e. g. earthworms) [37] serve as pollutant carriers. In the case of this last group, the transfer of pollutants deeper into the soil profile can take place indirectly (as a result of "transfer" of soil mass) [38] or directly (as a result of the accumulation in tissues or sorption on their surface) [8, 37]. In the experiment described, all the factors described above undoubtedly take some part in PAH transfer, and in order to state which plays the most significant role requires additional, more detailed, study.

Soil Organic Matter and PAH Leaching

In evaluating the fate of organic pollutants in the environment, we cannot skip the role of soil organic matter. As has already been mentioned, organic matter (e. g. dissolved organic carbon, DOC), can significantly influence PAH leaching [23, 29, 33, 34]. This issue is especially important in those soils fertilized with sewage sludge where the influence of organic matter is especially visible due to the large amount of it.

In order to determine relations between organic matter and the possibility of individual PAH migration, a statistical evaluation was carried out on the basis of correlation coefficients. Changes in PAH content were determined against a background of changes in the organic matter content in the 0-20 and 20-40 cm soil horizons — firstly, two days from the introduction of the sludge and then during the 18-month period of study.

Positive statistically significant relationships between PAH content in the 20-40 cm soil horizon and the TOC content in this horizon in the first phase of the experiment (two days after sludge introduction) were observed only in the case of naphthalene (0.806, $P \leq 0.05$), acenaphthylene (0.737), acenaphtene (0.692), fluorene (0.677) and phenanthrene (0.688) ($P \leq 0.10$). This indicates that in the initial period of the study, organic matter may play a certain role in the transfer of these compounds. These compounds are relatively soluble in water compared to the remaining PAHs, which could be one of the reasons for the above relationship.

In evaluating data presented in Tables 2 and 3, it should be noted that the difference between the naphthalene content in the 0-20 cm soil horizon and the 20-40 cm soil horizon was distinct in all experimental variants (similarly as in the case of 5- and 6-ring PAHs). At the same time, a positive and statistically significant correlation coefficient of TOC — naphthalene was calculated. Based on the above information, it can be assumed that in losses of naphthalene in sewage sludge-amended soil, volatilization plays a more important role than leaching of this compound deeper into a soil's horizons.

During the 18-month experimental period, the evaluation of changes in PAH content in relation to organic matter changes in individual soil horizons showed high frequencies of statistically significant ($P \leq 0.05$) relationships only in the control plot and a plot with a sludge dose of 300 t·ha^{-1}. In the case of the remaining doses, even though statistically significant correlations (between changes of individual PAHs and changes in the content of organic carbon) were noted, they were only occasional (< 3 PAHs for the sludge dose).

In the current experiment, the organic matter changes (primarily its mineralization and the release of PAHs adsorbed earlier) undoubtedly influenced the desorption range and transfer of pollutants. The lack of clear relationships between changes in individual PAH content and changes in the TOC (total organic carbon) content does not exclude the role of this latter parameter in the transportation of PAHs deep into the soil profile. However, this last issue requires further study over a wider range in order to establish the detailed characteristics of organic matter (first of all DOM) in individual experimental variants. Litz and Müller-Wegener [25] have suggested, however, that widely spread surfactants play a main role in the transportation of PAHs deep into the soil profile fertilized with sewage sludge. To confirm the results of their experiments, they quote the results obtained by Pestke et al. [39], who also showed the more significant influence of surfactants and biosurfactants in the "dissolution" of PAHs than did the role of dissolved organic carbon (DOC). However, in studies carried out earlier [40] on the determination of the relationship between changes in the content of the PAH sum (in the 20-40 cm soil horizon) and the content of organic carbon content (in the 0-20 cm soil horizon) during the whole experiment (experimental dates I-III), it was found that a decrease in the organic carbon content was accompanied by an increase in PAH content in cases of sludge doses of 30 and 150 t·ha^{-1} (correlation coefficients were -0.895 and -0.889 respectively, $P \leq 0.05$). This points to the influence of organic matter and, as has been indicated above, requires a more detailed study of its role in the PAH distribution in those soils fertilized with sewage sludge.

Conclusion

To summarize the results obtained in this study, it can be stated that even though a strong adsorbent (organic matter from sludge) was introduced, transportation of

PAHs deep into the soil profile was possible. However, the range of this transportation depends on the dose of sewage sludge applied. Within a few days of sludge application, the presence of PAHs was detected in the 20-40 cm soil horizon and, depending on the experimental variant, they increased with time. This points to the potential risk of groundwater pollution. Another observation obtained in this study is the confirmation of the release of the PAHs which were not leachable earlier (i. e. secondary PAHs) became capable of migrating deeper into the soil profile.

Acknowledgements

Financial support from the State Committee for Scientific Research (KBN, Warsaw, Poland), project No. 2 P04G 091 27 is gratefully acknowledged. P. Oleszczuk is granted by the Foundation for Polish Science.

References

1. BODZEK D., JANOSZKA B., DOBOSZ C., WARZECHA L., BODZEK M. Determination of polycyclic aromatic compounds and heavy metals in sludges from biological sewage treatment plants. J. Chromatogr. A **774**, 177, **1997**.
2. MANOLI E., SAMARA C. Occurrence and mass balance of polycyclic aromatic hydrocarbons in the Thessaloniki sewage treatment plant. J. Environ. Qual. **28**, 176, **1999**.
3. SMITH K. E., GREEN M., THOMAS G. O., JONES K. C. Behavior of sewage sludge-derived PAHs on pasture. Environ. Sci. Technol. **35**, 2141, **2001**.
4. BARAN S., OLESZCZUK P. The concentration of polycyclic aromatic hydrocarbons in sewage sludge in relation to the amount and origin of sewage purified. Pol. J. Environ. Stud. **12**, 523, **2003**.
5. BARAN S., BIELIŃSKA E. J., OLESZCZUK P. Enzymatic activity in an airfield soil polluted with polycyclic aromatic hydrocarbons. Geoderma **118**, 221, **2004**.
6. MALISZEWSKA-KORDYBACH B. Bioavailability of organic xenobiotics in the environment, Kluwer Academic Publishers, Netherlands, **1999**.
7. JONES K. C., STRATFORD J. A., TIDRIDGE P., WATERHOUSE K. S., JOHNSTON A. E. Polynuclear aromatic hydrocarbons in an agricultural soil: long-term changes in profile distribution. Environ. Pollut. **56**, 337, **1989**.
8. KRAUSS M., WILCKE W., ZECH W. Availability of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) to earthworms in urban soils. Environ. Sci. Tech. **34**, 4335, **2000**.
9. COUSINS I. T., GEVAO B., JONES K. C. Measuring and modeling the vertical distribution of semi-volatile organic compounds in soils: I: PCB and PAH soil core data. Chemosphere **39**, 2507, **1999**.
10. BARAN S., OLESZCZUK P., BARANOWSKA E. Degradation of soil environment in the post-flooding area. Content of polycyclic aromatic hydrocarbons (PAHs) and s-triazine herbicide. J. Environ. Sci. Health B **38**, 783, **2003**.
11. BARAN S., OLESZCZUK P. The content of polycyclic aromatic hydrocarbons in a light soil as a function of emission source. Roczn. Glebozn. **3**, 49, **2003**.
12. OLESZCZUK P., BARAN S. Concentration of polycyclic aromatic hydrocarbons in sewage sludge-amended soil (accepted to Commun. Soil Sci. Plant Anal.).
13. OLESZCZUK P., BARAN S. Preliminary investigation for forecasting the content of polycyclic aromatic hydrocarbons after soil fertilization with sewage sludge. Pol. J. Environ. Stud. **13**, 253, **2004**.
14. OLESZCZUK P., BARAN S. Optimization of ultrasonic extraction of polycyclic aromatic hydrocarbons from sewage sludge samples. Chem. Anal. **48**, 96, **2003**.
15. OLESZCZUK P., BARAN S. Application of solid-phase extraction to determination of polycyclic aromatic hydrocarbons in sewage sludge. J. Hazard. Matter. **113**, 237, **2004**.
16. KONONOVA M. M. Soil Organic Matter. Pergamon, Oxford **1966**.
17. KÖGEL-KNABNER I., TOTSCHE K. I. Sorption and desorption of polycyclic aromatic hydrocarbons (PAHs) to individual constituents of natural and contaminated soils. Proc. 16th World Congress of Soil Science, Montpellier, France **1998**.
18. CARMICHAEL L. M., CHRISTMAN R. F., PFAENDER F. K. Desorption and mineralization kinetics of phenanthrene and chrysene in contaminated soils. Environ. Sci. Technol. **31**, 126, **1997**.
19. CORNELISSEN G., HASSEL K. A., VAN NOORT P. C. M., KRAAIJ R., VAN EKEREN P. J., DIJKEMA C., DE JAGER P. A., GOVERS H. A. J. Slow desorption of PCBs and chlorobenzenes from soils and sediments: relations with sorbent and sorbate characteristics. Environ. Pollut. **108**, 69, **2000**.
20. PIGNATELLO J. J., XING B. Mechanisms of slow sorption of organic chemicals to natural particles. Environ. Sci. Technol. **30**, 1, **1996**.
21. WHITE J. C., HUNTER M., NAM K., PIGNATELLO J. J., ALEXANDER M. Correlation between biological and physical availabilities of phenanthrene in soils and soil humin in aging experiments. Environ. Toxicol. Chem. **18**, 1720, **1999**.
22. WHITE J. C., HUNTER M., PIGNATELLO J. J., ALEXANDER M. Increase in bioavailability of aged phenanthrene in soils by competitive displacement with pyrene. Environ. Toxicol. Chem. **18**, 1720, **1999**.
23. YANG Y., RATTÉ D., SMETS B. F., PIGNATELLO J. J., GRASSO D. Mobilization of soil organic matter by complexing agents and implications for polycyclic aromatic hydrocarbon desorption. Chemosphere **43**, 1013, **2001**.
24. GEJLSBJERG B., KLINGE C., SAMSOE-PETERSEN L., MADSEN T. Toxicity of linear alkylbenzene sulfonates and nonylphenol in sludge-amended soil. Environ. Toxicol. Chem. **20**, 2709, **2001**.
25. LITZ N., MÜLLER-WAGENER U. The influence of surfactants applied by sewage sludge on the behaviour of atrazine and PAHs in semiarid soils. Z. Pflanzenernähr. Bodenk. **161**, 255, **1998**.

26. CESARE D. D., SMITH J. A. Surfactant effects on desoprtion rate of nonionic organic compounds from soils to water. Rev. Environ. Contamin. Toxicol. **134**, 1, **1994**.
27. OLESZCZUK P. Application of surfactants and biosurfactants in removal of persistent organic pollutants and petroleum hydrocarbons from soil. Roczn. Glebozn. **53**, 61, **2002** (in Polish).
28. KIM Y. J., OSAKO M. Leaching characteristics of polycyclic aromatic hydrocarbons (PAHs) from spiked sandy soil. Chemosphere **51**, 387, **2003**.
29. PETRUZZELLI L., CELI L., CIGNETTI A., MARSAN F. A. Influence of soil organic matter on the leaching of polycyclic aromatic hydrocarbons in soil. J. Environ. Sci. Health B **37**, 1, **2002**.
30. TEBAAY R. H., WELP G., BRÜMMER G. W. Gehalte an polycyclischen Aromatischen Kohlenwasserstoffen (PAK) und deren verteilungmuster in unterschiedlich belasteten böden. Z. Pflanzenernähr. Bodenk. **156**, 1, **1993**.
31. WEIGAND H., TOTSCHE K. U., KÖGEL-KNABNER I., ANNWELLER E., RICHNOW H. H., MICHAELIS W. Fate of anthracene in contaminated soil: transport and biochemical transformation under unsaturated flow conditions. Europ. J. Soil Sci. **53**, 71, **2002**.
32. KIM I. S., PARK J. S., KIM K. W. Enhanced biodegradation of polycyclic aromatic hydrocarbons using nonionic surfactants in soil slurry. Appl. Geochem. **16**, 1419, **2001**.
33. MARSCHNER B. DOM-enhanced mobilization of benzo [a] pyrene in a contaminated soil under different chemical conditions. Phys. Chem. Earth **23**, 199, **1998**.
34. RABER R., KÖGEL-KNABNER I. Influence of origin and properties of dissolved organic matter on the partition of polycyclic aromatic hydrocarbons (PAHs). Europ. J. Soil Sci. **48**, 443, **1997**.
35. MCCARTHY J. F., ZACHARA J. M. Subsurface transport of contaminants. Environ. Sci. Technol. **23**, 496, **1989**.
36. JENKINS M. B., LION L. W. Mobile bacteria and transport of polynuclear aromatic hydrocarbons in porous media. Appl. Environ. Microbiol. **59**, 3306, **1993**.
37. BELFROID A. C., SEINEN W., VAN GESTEL K. C. A. M., HERMENS J. L. M., VAN LEEUWEN K. J. Modelling the accumulation of hydrophobic organic chemicals in earthworms. Environ. Sci. Pollut. Res. **2**, 5, **1995**.
38. MÜLLER-LEMANS H., DORP H. Biotrubation as a mechanism for radionuclide transport in soil: relevance of earthworms. J. Environ. Radioactivity **31**, 7, **1999**.
39. PESTKE F. M., BERGMANN C., RENTROP B., MAAßEN H., HIRNER A. V. Mobilisierbarkeit von hydrophoben organischen schadstoffen in belasteten böden und abfällen. Acta Hydrochim. Hydrobiol. **25**, 242, **1997**.
40. BARAN S., OLESZCZUK P. The risk of PAHs leaching from sewage sludge-amended soil. Proc. Conf. Micropollutants in the environment, Polit. Częst., Częstochowa **2003**.