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A STUDY OF MIGRATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN A SEWAGE SLUDGE–SOIL SYSTEM

Sewage sludge can be used as a fertilizer in agricultural production. However frequent occurrence of dangerous contaminants such as polycyclic aromatic hydrocarbons (PAHs) due to their toxic potential, makes this technology controversial. The persistence and migration ability of PAHs in the sewage sludge–soil system was investigated. The results show that sewage sludge applications may cause an increase in migration of some marked compounds in the soil profile. Therefore it is important to perform a close monitoring of PAHs content during the sewage sludge fertilization procedure.

1. INTRODUCTION

According to data published by the Polish Central Statistical Office in 2000–2010, the total production of sewage sludge in Poland ranged from 895.1 to 1124.4 thousand tons of dry matter [1]. Such a large amount of waste and its diverse composition makes it difficult to manage [2, 3]. One of green technologies employed in sewage sludge management is its use as fertilizer in agricultural production. However, despite many benefits, this technology brings a lot of risks primarily associated with the presence of dangerous organic and non organic pollution within this material [4–6].

Some of the most important organic contaminants often found in sewage sludge are polycyclic aromatic hydrocarbons (PAHs), contaminants containing in the molecule at least two aromatic rings without any substituents. The origin of these compounds may be natural but their presence is caused mainly by human activity. Companies classified as heavy industry belong to the most important source of PAHs. This situation takes place because PAHs are formed during incomplete combustion of all

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hydrocarbons (except methane) and in other high temperature processes involving organic matter [7–9]. To group of PAHs contains ca. 200 compounds but for scientific purposes the American Environmental Organization (US EPA) recommends only sixteen to be determined: acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene dibenzo(a,h)anthracene, fluoranthene, fluorine, indeno(1,2,3-c,d)pyrene, naphthalene, phenanthrene, pyrene [7, 10].

PAHs content in sewage sludge is heavily dependent on many factors. The most important are [11]:

- density and nature of the industry in the area from which wastewater is collected,
- methods of water treatment procedures,
- degree of hydration of sewage sludge,
- season and weather conditions.

The results of research conducted by Oleszczuk et al. [6, 10–12] and Włodarczyk-Makuła [13] showed that the PAHs content in sewage sludge ranged from 0.002 to 20 mg/kg dry weight.

Some of the most important problems associated with the usage of sewage sludge as a fertilizer are the possibility of permanent binding of organic pollutions on soil particles and potential ability of migration of these compounds into the deeper layers of soil. Both of these phenomena may have a negative influence on the total soil condition. The first may cause long-term contamination, while the latter potentially contributes to migration of hazardous substances into the environment [6, 11]. Research conducted by Oleszczuk showed that addition of sewage sludge into soil has serious influence on both physicochemical properties and soil microbial activity. The scale and nature of these processes are strongly dependent on the type of soil, its physicochemical properties, the physicochemical properties of sewage sludge and of the amount and dosing frequency of fertilizer [10–12].

The aim of the current paper was to investigate the migration ability of selected polycyclic aromatic hydrocarbons such as fluorene, fluoranthene and benzo(a)pyrene in sewage sludge–soil system.

2. METHODS AND MATERIALS

During the laboratory experiment, six columns 32 cm long and 10 cm in diameter were filled with loamy soil delivered from agricultural land located near Częstochowa (Table 1). The soil was introduced according to the soil profile.

Then the columns 3–6 were additionally filled with sewage sludge delivered from the municipal wastewater treatment plants located in the region of Częstochowa (Table 1). The sewage sludge dose was calculated according to the recommendations of the ministerial decree of 13 July 2010 regarding municipal sewage sludge

(Dz.U. 10.137.924). The dose was 100 g per column. Into the 2nd, 5th and 6th column, the mixture of three PAHs (50 cm^3 each): fluorene (0.0033 g/50 cm^3 of methanol), fluoranthene (0.0033 g/50 cm^3 of methanol) and benzo(a)pyrene (0.0005 g /50 cm^3 of methanol) was also added.

Table 1

Physicochemical properties of soil and sewage sludge

Type of material	Soil loamy sand	Sewage sludge for agricultural use after stabilization
Dry weight, %	99	35
pH (in H_2O)	5.865	7.597
pH (in KCl)	4.733	6.841
CEC, mmol/kg	6.25	no data
TOC, g/kg	10.59	215
TC, g/kg	13.010	302
P, mg/kg	196	277
N, g/kg	1.157	18.4
Cd, mg/kg	0.38	56.44
Pb, mg/kg	27.06	212.21
Zn, mg/kg	67.07	2730.7

CEC – cation exchange capacity, TOC – total organic carbon, TC – total carbon.

Both soil and sewage sludge were examined in terms of PAHs content. Preparation of samples for the PAHs determination was carried out by the solid–liquid phase extraction with a 2-propanol in an ultrasonic bath. Then, after centrifugation and filtration, samples were subjected to concentration and purification using SPE columns. For this purpose, Chromabond EASY 6 cm^3 columns were used. The relevant part of the analysis was conducted using high performance liquid chromatography (HPLC), THERMO Scientific HPLC system consisting of a pump P4000, autosampler AS3000 and UV-Vis detector UV2000. PAHs were separated on Restek Pinnacle® II PAH 4 µm, 150 × 10 mm column by using the gradient elution technique. As for the mobile phase mixture of water, methanol and acetonitrile were used. The results were gathered by using UV-Vis detector setup (λ = 254 nm). As a standard Restek 610 PAH calibration Mix A was used.

Such prepared columns were transferred into a large-sized phytotron chamber and left for 3 months. Incubation was conducted at 20–22 °C and 90% humidity. During this time, each column was watered with 150 cm^3 of distilled water 2 times per week. After incubation, the samples for determination of PAHs content were collected from every 5 cm layer of each column and secondary PAHs analyses were conducted.

All methods and techniques used in this paper were based on those recommended by the manufacturer of chromatography products, Restek LC columns, Macherey-Nagel SPE columns, and on the standards and methods available in papers from the Philadelphia list [11, 14, 15].

3. RESULTS

3.1. DEGRADATION OF PAHs

The results determination of PAHs content in sewage sludge conducted before incubation (Figs. 1, 2) show that used waste was heavily contaminated. Total PAHs concentrations within this material varied from 4465 to 5187 μg/kg.

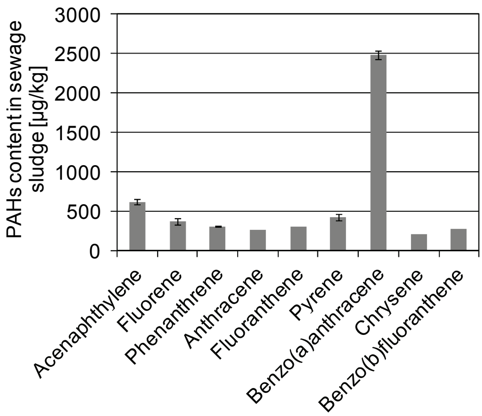

Fig. 1. PAHs content in sewage sludge

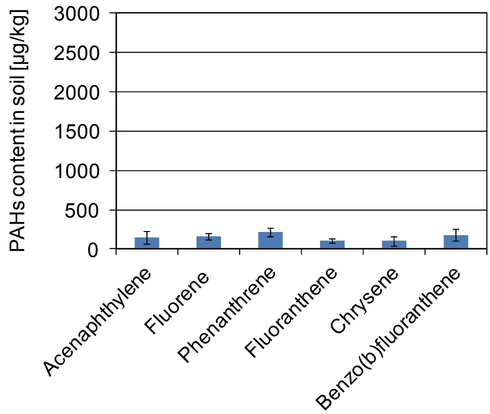

Fig. 2. PAHs content in soil

PAHs were found at significant concentrations also in the soil used for experiment. Total PAH content in these samples was in the range of 875 to 934 μg/kg. According to classification proposed by Maliszewska-Kordybach [16] such soil can be classified as PAHs contaminated soil (total PAH 600–1000 μg/kg).

A common phenomenon observed in all columns during the three months of incubation was the decreasing the concentrations of most marked compounds, independently on soil depth. The largest reduction of total PAHs contents occurred in columns 3, 4 (the soil mixed with PAHs) and 5, 6 (the soil mixed with sewage sludge and PAHs) (Fig. 3). PAHs introduced as a mixture shown lower stability then PAHs delivered in soil and sewage sludge. The proportional representation of degradation of the degree of PAHs mixture (fluorene, fluoranthene and benzo(s)pyrene – columns 2, 5, 6) is shown in Fig. 4.

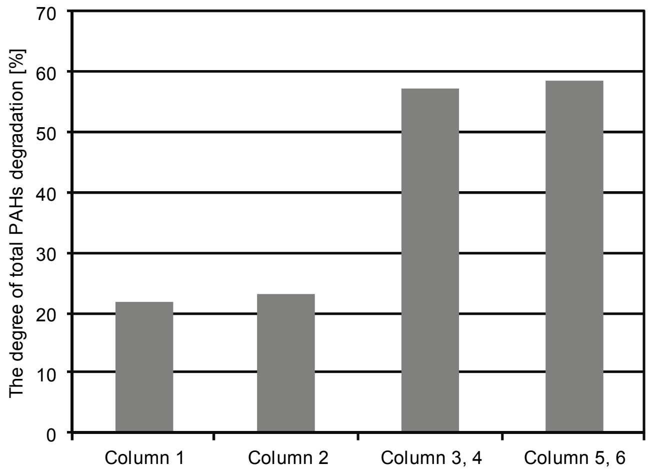

Fig. 3. The degree of total PAHs degradation in each column

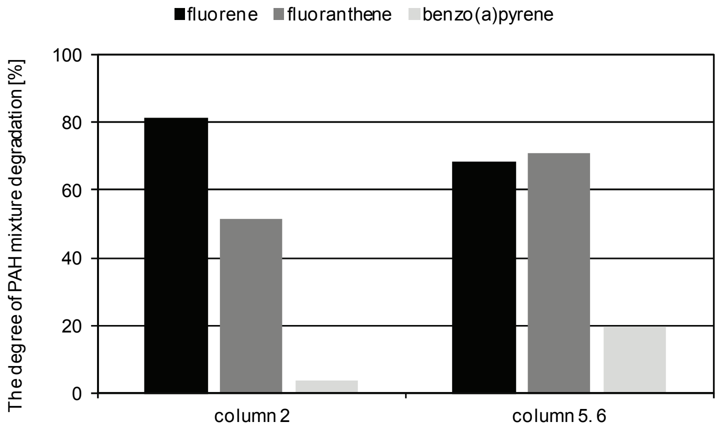

Fig. 4. The degree of PAH mix degradation in columns 2, 5 and 6

3.2. PAHs MIGRATION

In the control sample – column 1, filled only with soil (Fig. 5), concentrations of individual PAHs after incubation were quite different. The wide variation in the results obtained from this sample was caused by relatively low concentrations of each marked compound. In this sample, the total PAHs concentration was the lowest from all of the prepared samples. The highest PAHs content – 33.6% of all extracted compounds, was in the first 5 cm layer of this column. The lowest concentrations of this pollution – 7.6% of all extracted compounds, was found in the deepest layer – 30 cm, respectively.

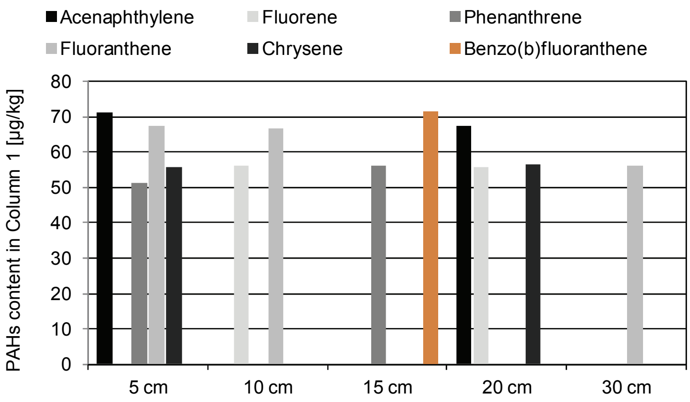

Fig. 5. PAH migration in the control sample; column 1

In column 2, soil with three PAHs, the total PAH content was highest from all evaluated samples. In this sample, a high relation between column depth and PAH content was observed – total PAH concentrations were decreasing with the column depth. Concentrations of individual compounds obtained after incubation are shown in Fig. 6. The highest amount of PAH, 36.3% of all compounds extracted from this column, was found in the first 5 cm layer of the column. The lowest values, 6.9% of all compounds extracted from this column, was noted in the last 30 cm layer. In this layer acenaphtylene, fluorine, phenanthrene, chrysene and benzo(b)fluoranthene were not dectected in contrast to upper layers.

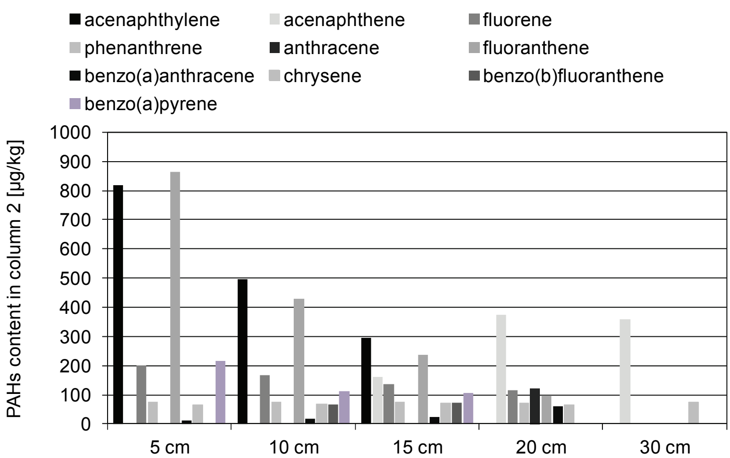

Fig. 6. PAH migration in a sample with soil and PAH mixture; column 2

The average values of PAHs content in columns 3 and 4, soil with sewage sludge, are presented in Fig. 7. Results obtained from this samples show that PAH concentrations were not correlated with the depth of the column. The values of total PAH concentrations in all layers except the last one, 30 cm, were quite similar and remain in the range of 17–27% of all extracted compounds from this sample. Only in the last layer decrease of the total PAHs content was noted. However, in the second, 10 cm layer an increase of concentrations of some PAHs (acenaphthylene, phenanthrene, fluoranthene, pyrene, benzo(a)anthracene, chrysene) was observed. It was probably caused by the fact that sewage sludge was mixed with a 5 cm surface layer of column which in turn could lead to direct contact of this material with the second, 10 cm, layer of column, and some compounds could migrate.

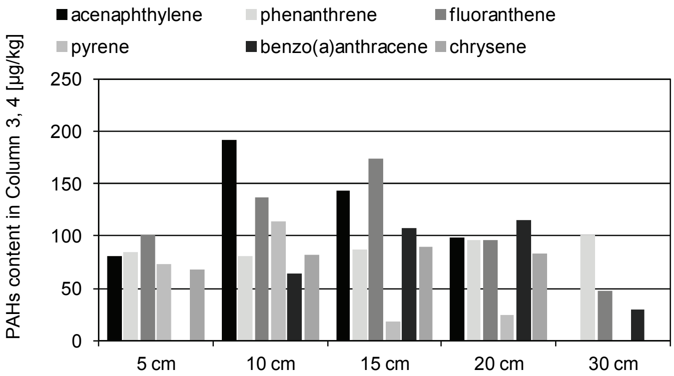

Fig. 7. PAH migration in samples 3 and 4 (average values)

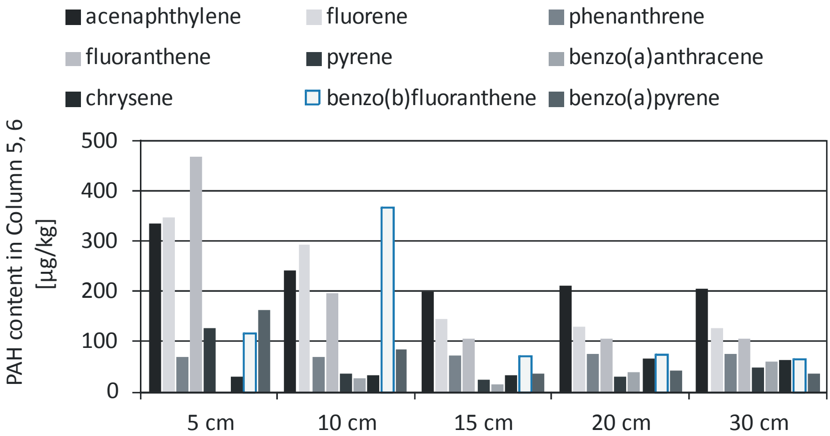

Fig. 8. PAH migration in samples 5 and 6 (average values)

When soil was mixed with sewage sludge and three PAHs (columns 5 and 6), the concentrations of PAHs after incubation depended on their origin (Fig. 8). The highest levels were detected for PAHs introduced in the form of a mixture (fluorene, fluoranthene and benzo(a)pyrene). Their concentrations decrease with the column depth. In the case of other compounds, concentrations were similar to those in columns 3 and 4 (soil with sewage sludge) were observed.

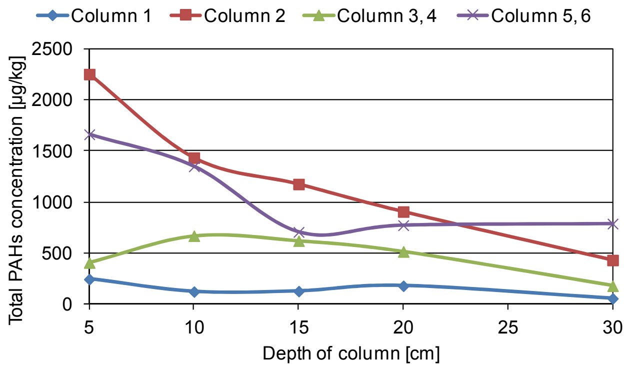

Fig. 9. Total PAH migration content in all samples

In Figure 9, the dependences of total concentrations of PAHs in all columns on the column depth are presented. The depth dependent reduction of PAHs content was observed in columns with three PAHs mixture – columns 2, 5 and 6. In columns with sewage sludge, the degree of total PAHs reduction was smaller and much lower than in columns with three PAHs. PAHs delivered from sewage sludge in few cases show the ability to penetrate the soil profile. In all six samples, except columns 3 and 4, the highest values of extracted compounds were in the upper 5 cm layer of the column. The lowest values of total PAHs content, in all columns, were in the depthless (30 cm) soil layer.

4. DISCUSSION

The highest degree of PAHs degradation was observed in the columns containing the addition of sewage sludge. It was likely due to creation of favorable conditions for the development of soil microorganisms such as bacteria or fungi [9, 11]. Addition of sewage sludge to the soil caused a rapid increase of soil moisture which promoted the development of all organisms. Simultaneously it provided a large dose of nutrients in the form of both organic matter and non-organic compounds. The sludge also contained a larger pool of exogenous organisms in relation to the soil microflora which led to an increase in the quantity and viability of bacteria or other organisms capable of degrading organic pollutants such as PAHs [12]. The addition of sludge also led to an increase in the frequency of the occurrence of chemical reactions in the soil which promoted the process of abiotic degradation of PAHs [9, 11, 17].

The data on PAHs migration in the soil profile showed that the compounds naturally present in sewage sludge have a better ability to penetrate the soil profile than those in a mixture. It was caused by the fact that PAHs introduced in the form of a mixture were not bound to any form of soil particles or any other organic and innorganic soil materials. This directly resulted in the immobilization of these substances within the upper layers of soil profile. PAH compounds are not soluble in water [7], therefore their migration in samples containing sludge was caused by the phenomenon of co-migration with the so-called soluble mobile organic fraction. Due to the high organic matter and high moisture content of the introduced sludge, the creation of a mobile water-soluble fraction of organic compounds was observed. That phenomenon may influence the ability to transfer organic contaminants such as PAHs on the principle of co-migration [11, 18].

The increased mobility of some PAHs in columns 3–6 may also be caused by co-migration with exogenous microorganisms introduced into soil with sewage sludge. Some of bacteria strains have the ability to absorb organic pollutions and transport them [9, 11].

5. CONCLUSIONS

The results of the study indicate that the land application of sewage sludge may have a negative effect on the overall condition of the soil, which increases in a given time period. Depending on the dosing frequency and the degree of contamination of the used material, this procedure may lead to permanent soil contamination by organic pollutants such as PAHs. It can also lead to the spread of these contaminants with insoluble organic matter which in turn poses a risk to the nearest surface water.

However, on the other hand, the addition of sewage sludge can accelerate the processes of both biotic and abiotic degradation of high concentration of organic contaminants present in soil.

Therefore, it is important to perform a close monitoring of PAHs contents, during the sewage sludge fertilization procedure. It is also important to conduct a more detailed study of the PAHs migration mechanisms in order to obtain data to make changes in existing legislation to ensure full safety of the procedure of agricultural sewage sludge use.

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