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ELUTION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) FROM TWO COMPOSTS

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Abstract: Composts made of municipal solid waste could be widely used in reclamation of soil-less mechanically transformed grounds. Even though its usefulness, bearing in mind its origin, it is necessary to consider the compost composition in order to avoid posing a threat to environment due to the possible emission of toxic substances which could be present in compost. Especially, organic waste should be monitored, because being present in composts it might be leached and pose a risk to groundwater and plants. In this work the leaching tests were carried out to state the solubility of polycyclic aromatic hydrocarbons in water. The both tests results show low solubility of PAHs, max. 10.4% in lysimetric test and 3.9% in one-step leaching test.

INTRODUCTION

The increasingly growing number of municipal waste forces us to selective waste collection, and afterwards introducing recycling and neutralizing technologies. One of the means of reducing the amount of waste is a composting process [6]. It is an oxygen-requiring microbiological process, which transforms organic compounds, occurring in municipal waste, into compost. The dominant processes are mineralization, which is a decomposition of organic compounds from waste, and humification – a multimolecular synthesis of humus compounds, which afterwards are part of compost [10]. Micro-organisms participating in the process are mostly mesophilic and thermofilic bacteria as well as Actinomyces and fungi [3]. Exothermic compost process leads to hygienisation of the creating compost ensuring safety turnover of the ready product. Composts are made according to different technologies varying, among others, in its source basis. As far as non-segregated municipal wastes are concerned, only organic fraction, sectioned from a stream of waste, can be subjected to the composting process. Developing compost contains significant amount of organic matter (about 40%) and can be used in the land reclamation processes in mining areas, where the land became geomechanically transformed or in soil-less grounds. However, bearing in mind the possible content of harmful substances in composted waste, its amount in ready product should be checked due to the fact that the harmful substances being subjected, for example to micro-organisms [8] or weather conditions, might get released or migrate with water into the ground-soil environment posing a risk to underground water, plants and, indirectly, to human. The possibility of leaching out the chemical elements or compounds depends not only on solubility of a given substance in

water, but also on the existence of other accompanying compounds, which can either increase or decrease the intensity of the process and the characteristics of a matrix. Some of the most common organic micropollutants, occurring in the environment, are polycyclic aromatic hydrocarbons (PAHs) [1]. Those compounds occurring in the compost create the possibility of using it as fertilizer or as a surface in land reclamation process. Those hydrocarbons are decomposed either by photochemical or microbiological processes. However, pentacyclic and six-cyclic PAHs display considerable resistance to degradation [9]. The aim of the paper is to establish the degree of polycyclic aromatic hydrocarbons (PAHs) elusion from compost made of municipal waste as templates with high content of organic substances.

MATERIALS AND METHODS

Materials

The research was done on a sample of ripen compost, made of non-segregated, (according to the MUT-DANO technology) municipal wastes and on samples of organic fraction isolated from municipal waste, obtained according to MUT-Herhof technology. The compost samples were dried and sieved through a sieve with 2 mm diameter mesh. With the aim of establishing the basic parameters of the analyses template, the reaction, electrolytic conduction, and organic substance content analysis were carried out (Tab. 1).

Table 1. Average content of organic substance and PAH in composts (n = 3)

	Herhof (< 2 mm)	DANO
Organic matter [%]	32.4 ± 1.80	(< 2 mm) 36.3 ± 4.11
		(> 2 mm) 52.9 ± 1.92
PAH [μg/kg d.w.]	27.3 ± 6.26	(< 2 mm) 134 ± 21.03
		(> 2 mm) 106 ± 17.84

Methods

Organic matter was analyzed by weight method after burning at 600°C. The experiments included polycyclic aromatic hydrocarbons elution in the lysimetric test (for DANO compost) and one-step leaching test (for the Herhof compost). Spiking of compost samples was made with qualified standards from LGC Promochem. The standard solution containing 16 PAHs in benzene and hexane (1:1 v/v) solvent according to US-EPA, was applied using syringe, being spread into the composts samples (air dry); afterwards the prepared templates were stabilized without light access and in the temperature of about 5°C for three hours, $25 \cdot 10^{-6}$ dm^3 of the standard containing 5 μg of each of 16 compounds, was injected into the samples of Herhof compost and $50 \cdot 10^{-6}$ dm^3 of standard, containing 10 μg of each of 16 compounds, was spread into the samples of DANO compost. In this way, the amount of PAHs per kilo of compost was 1.67 and 5.0 mg of each compound respectively. Two different PAHs levels were used to save natural differences which usually occur between PAH levels in two analyzed compost samples. Lysimetric leaching test was carried out in glass lysimetres (55 x 33 mm) fitted with glass sinter G4 filled-up with dry compost. Leaching test was performed using distilled water (pH 5.8,

EC 4.7 μS/cm) (in a quantity corresponding to one month rainfall in Poland) for about 30 minutes. One-step leaching test was carried out through shaking out with distilled water (by a ratio of compost: water = 1:10) for 12 hours, without daylight access, in electronically stabilized temperature 20°C. PAHs extraction from elute was carried out with the usage of hexane HPLC-grade for 4-hour shaking out. Polycyclic aromatic hydrocarbons (PAHs) were determined in unrefined hexane extracts by a GC-FID (Varian series 3800) method using capillary column ZB-5 (30 m x 0.25 x 0.25 μm film thickness) and stable flow of helium through a column in an amount of 1 cm^3/min. Parameters of analysis: injector temperature – 250°C, detector temperature – 300°C, oven temperature – 100°C for 2 minutes, after then rate 5°C/min to 300°C – held for 10 minutes. During work a split injection mode was used. Recoveries levels for this procedure were low for naphthalene (41–55%), and higher (73–91%) for the rest of individual PAHs. Each sample was analyzed in triplicate (n = 3). The detection limit was 0.2–0.5 ng per individual compound. LGC Promochem Corporation from UK produced qualified standards (2000 $\mu g/cm^3$ of each analyte) for calibration curve. Correlation coefficient was calculated for a curve of linear model $y = ax + b$, and the analysis of variance were carried out by the LSD test. Moreover, in order to define the origin of determined compounds, the PAHs concentration ratio: ANT/(ANT+PHE), BaA/(BaA+CHR), FLT/(FLT+PYR) was calculated [2]. Also blind test was carried for natural level of PAHs leaching from both types of composts determination (Tab. 1).

RESULTS AND DISCUSSION

The compost samples obtained by the Herhof method showed a significant amount of diversed course-grained fraction, and due to that fact only fine fraction (diameter < 2 mm) was analyzed. Organic substance content in fine-grained fractions was very similar in both samples; however it was much higher in coarse-grained fraction reaching nearly 52% (Tab. 1). PAHs content in control samples of both compost types was not high. Especially low concentration was noted in the Herhof compost made of organic waste. The content of those compounds was over three times lower than that of DANO compost (Tab. 1). The noted values were not high, because wooden waste grounded for compost contained approximately 700 μg/kg [4], while the compost made of green waste contained around 650–655 μg/kg [5]. Organic waste compost might contain PAHs in an amount even 10 times higher than observed in this paper, reaching the concentration of 1715 μg/kg d.w. [2]. Significant part of mineral fraction is fine-grained (dust, sand) and slightly higher content of PAHs in fraction < 2 mm with a lower content of organic fraction.

Water extract taken from the Herhof test sample contained only six compounds from the studied group, out of which fluoranthene constituted the highest part (30%), while the lowest was phenanthrene (2%) (Tab. 2). In extract taken from DANO test sample, benzo(a)pyrene had the highest content, while benzo(a)anthracene the lowest. DANO samples do not only have three times more PAHs than Herhof samples, but contain as much as 12 compounds out 16 that were examined (there were only 6 in Herhof samples), and the most often occurring compound was benzo(a)pyrene (28.3% of content). It leads to conclusion that the compound is brought along with inorganic fractions, which are in municipal waste stream and get into the final product.

Table 2. Average content of PAH's in Herhof and DANO control samples proceed in blind test [%] (n = 3)

Compound	Herhof	DANO
Naphtalene	17.4 ± 4.8	7.4 ± 0.5
Acenaphtylene	nd	1.8 ± 0.8
Acenaphtene	nd	2.5 ± 1.6
Fluorene	7.2 ± 0.9	4.7 ± 0.4
Phenanthrene	2.1 ± 1.0	9.7 ± 4.0
Anthracene	24.3 ± 2.4	7.3 ± 1.6
Fluoranthene	28.6 ± 2.8	21.4 ± 5.1
Pyrene	nd	12.5 ± 4.2
Benzo(a)anthracene	nd	1.5 ± 0.3
Chrysene	nd	2.9 ± 1.5
Benzo(k)fluoranthene	20.4 ± 6.6	nd
Benzo(a)pyrene	nd	28.3 ± 8.5

nd – not detected

The calculated ratio of each hydrocarbon was [2] ANT = 0.43, BaA = 0.34, and FLT = 0.63 for DANO sample, and ANT = 0.53 for Herhof sample. Those relationships show the predominance of pyrogenic PAHs origin in both examined sample series [2]. This could be an effect of dust sedimentation during compost maturation process in open air.

Hydrocarbon elution from Herhof compost samples showed quite significant differences in each hydrocarbon content in water (Fig. 1).

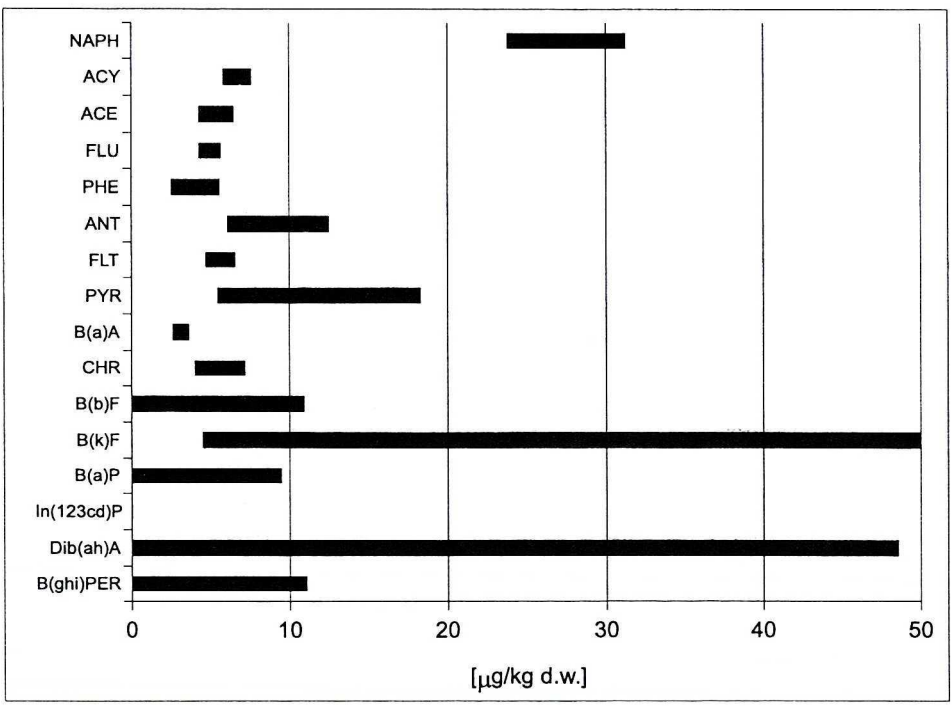

Fig. 1. The number of PAH eluted from Herhof sample compost (n = 3)

High amount of benzo(k)fluoranthene, dibenz(a,h)anthracene, naphthalene, and benzo(ghi)perylene has been noticed. Concentrations in the remaining examined hydrocarbons were not high and took average value from 3.1 μg/kg d.w. for benzo(a)anthracene to 11.7 μg/kg d.w. for pyrene. Indeno(1,2,3-cd)pyrene was not detected in the elutes. In accordance with the figures referring to solubility of those compounds in water [7], there was an assumption that there will be high concentration of naphthalene, acenaphthene and acenaphthylene. There were highly significant correlations ($r = 0.67$, $r = 0.95$) between the amount of PAHs leached from DANO and Herhof samples in blind tests. In the case of the tests enriched by PAH's injection, even though a correlation between total amount of leachable PAHs has been noticed, the concentration of PAHs elutes was more diversified, what is proved by previously noted statistical significant difference ($p < 0,05$) between results of two tests. Taking into consideration the initial amounts of PAHs in samples, the highest leaching degree in water phase was noted for benzo(k)fluoranthene 3.9%, while the average leaching degree was 1.15% for all 16 PAHs. Benzo(a)pyrene sorption was high and was above 99% which was observed well in the case of argillaceous deposit with high sorption complex [1].

In the case of DANO compost, fractions below and above 2 mm in diameter with diversified organic substance content were examined separately. For coarse-grained fraction, the highest leaching (average 273.0 μg/kg d.w.) was noted for benzo(k)fluoranthene

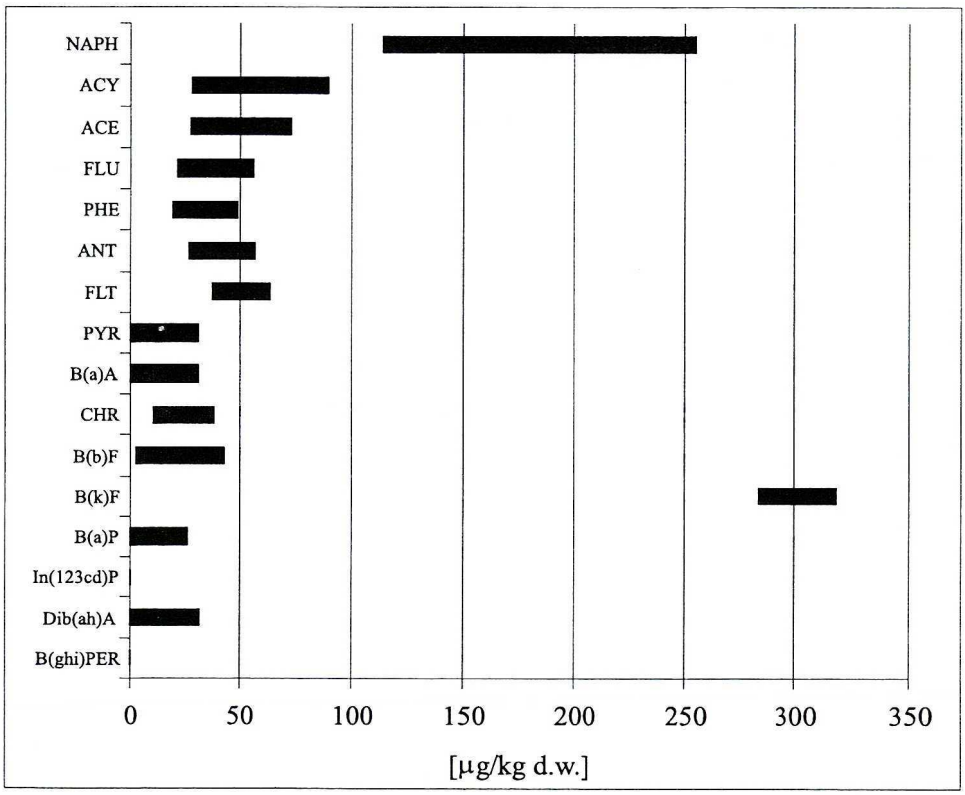

Fig. 2. The amount of PAHs eluted form compost DANO samples, fraction < 2 mm (n = 3)

and for naphthalene (average 107.7 μg/kg). The remaining hydrocarbons were eluted in lower degree – average from 14 μg/kg d.w. for benzo(k)fluoranthene to 52.3 μg/kg d.w. for acenaphthylene. Six-cyclic PAHs: indeno(1,2,3-cd)pyrene and benzo(ghi)perylene were not detected in elutes. As in the case of Herhof samples, the highest concentration of easily-leaching hydrocarbons was for naphthalene (max. 254.2 μg/kg d.w.). In spite of comparatively small leachability in water (0.55 μg/dm^3) [11] the highest mobility was observed for benzo(k)fluoranthene, which occurred in significant amounts of elutes in all performed tests (Fig. 2).

For fine-grained fractions, as for the coarse-grained fractions, the highest leaching, average 303.5 μg/kg, was noted for benzo(k)fluoranthene and for naphthalene, average 162.9 μg/kg d.w.

The remaining hydrocarbons eluted in lower degree – average from 8.7 μg/kg d.w. in the case of benzo(a)pyrene to 56.8 μg/kg d.w. for acenaphthylene. There were no six-cyclic PAHs: indeno(1,2,3-cd)pyrene and benzo(ghi)perylene. Despite significant differences in organic matter, the results of hydrocarbon elution in the case of both granulometric fractions of DANO compost had similar character. The only exception was benzo-(k)fluoranthene, for which, in the coarse-grained fraction (> 2 mm), higher scattering of concentration than in fine-grained fraction was noticed. The most highly connected with the still matter samples seem to be five- and six-cyclic hydrocarbons, which were not detected in elutes. Only in the case of one-step leaching test (Herhof compost) benzo(ghi) perylene occurred (Fig. 3).

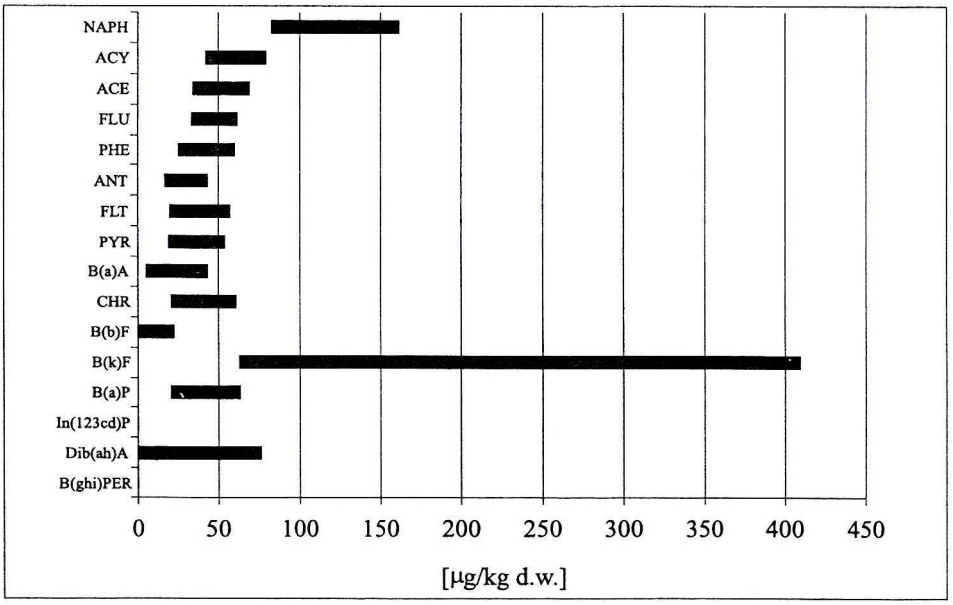

Fig. 3. The amount of PAH eluted from compost DANO samples, fraction > 2 mm (n = 3)

In the case of DANO samples highly statistically significant correlations were observed (r = 0.90–0.99) between the amount of leaching PAHs and for fine-grained fractions. Coarse-grained fraction displayed higher diversity and even though the significant correlation has been noted (r = 0.87), the insignificant coefficient of correlation (r = 0.21) was

observed as well. There were no statistically significant differences between the amount of PAHs leached from DANO samples, both fine- and coarse-grained, and correlation calculated for those series of samples were high and was r = 0.97. Sorption of benzo(a)pyrene in the case of two fractions of DANO samples was high and was 97.8% for coarse-grained fraction and over 99% for fine-grained fraction. It shows that this compound is highly bound with samples of mineral fraction, whose content in the case of fine-grained fraction of both series was over 60%.

Taking into consideration the amount of injected PAHs in DANO tests, the highest leaching degree was noted, as it was in the case of compost Herhof samples, for benzo(k)fluoranthene 10.4%, whereas average leaching degree for both granulometric fractions of DANO compost was 1.98%. This value is slightly higher than in Herhof samples (1.15%); however it can be caused by higher PAHs amount (5 mg/kg) that was injected into the samples.

CONCLUSION

The water extract obtained by one-step leaching test of compost made according to MUT-Herhof contains by average 4.3 times less polycyclic aromatic hydrocarbons (PAHs) than the extract from compost made according to MUT-DANO.

On the basis of calculations of mutual ratio of the examined compounds, it can be said that polycyclic hydrocarbons existing in both sample series (Herhof and DANO) origin mostly from pyrogenic processes, which could be the effect of enrichment of exanimate material during maturation process. In lysimetric test of DANO compost, benzo(k)fluoranthene eluted in highest degree (10.4%), while the lowest elution was for six-ring hydrocarbons – indeno(1,2,3-cd)pyrene, and benzo(ghi)perylene which were not found in elutes. In one-step leaching test of Herhof compost, benzo(k)fluoranthene eluted in the highest degree (3.9%), while the lowest elution was for indeno(1,2,3-cd)pyrene which was not found. What is especially interesting is a strong sorption of toxic benzo(a)pyrene on the level of 97.8–99.5% merits attention, while the lower degrees were noted for samples with higher organic matters. There was no correlation found between the content of organic matter in composts samples and the PAHs amount determined in water elute.

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ELUCJA WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH (WWA) Z DWÓCH RODZAJÓW KOMPOSTÓW

Komposty uzyskiwane z odpadów komunalnych mogą znaleźć szerokie zastosowanie w gospodarce człowieka m.in. do rekultywacji gruntów bezglebowych, czy też przekształconych geomechanicznie. Ze względu jednak na swoje pochodzenie należy zwrócić szczególną uwagę na ich skład tak, aby nie narażać środowiska na emisję szkodliwych substancji, które mogą znajdować się w kompostach. Na szczególną uwagę zasługują zanieczyszczenia organiczne, które znajdując się w kompostach mogą być wymywane, a przez to stwarzać zagrożenie dla wód gruntowych i roślin. W pracy wykonano testy wymywalności służące określeniu możliwości rozpuszczania się wielopierścieniowych węglowodorów aromatycznych w wodzie. Testy wykazały niską wymywalność WWA zarówno w teście lizymetrycznym (maksymalnie 10,4%) jak i w jednostopniowym teście wymywalności (3,9%).