Proceedings of ECOpole
DOI: 10.2429/proc.2015.9(1)018 2015;9(1)

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CONTENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL FERTILIZED WITH ORGANIC MATERIALS DERIVED FROM WASTE

ZAWARTOŚĆ WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W GLEBIE NAWOŻONEJ MATERIAŁAMI ORGANICZNYMI POCHODZENIA ODPADOWEGO

Abstract: The aim of the research was to determine the influence of fertilization with waste organic materials on the content of polycyclic aromatic hydrocarbons (PAHs) in soil. Samples obtained in the third year of the field experiment were analysed. The field experiment comprised 7 treatments: a non-fertilized soil and a soil fertilized with mineral fertilizers, cattle manure, green waste compost, sewage sludge, compost from sewage sludge and straw as well as with a mixture of sewage sludge and hard coal ash. Maize, which was cultivated for silage, was the test plant. The content of 16 compounds belonging to the group of polycyclic aromatic hydrocarbons (according to the list of the United States Environmental Protection Agency) in the soil was determined using gas chromatography with mass detection, after solid phase extraction. The total content of the 16 PAHs was lower in the soil fertilized with manure and compost from sewage sludge and straw than in the control soil, and higher in the soil fertilized with green waste compost as well as with the mixture of sewage sludge and ash. It was determined that the PAHs content in the soil of the two remaining treatments was close to the content found in the non-fertilized soil. 4-ring compounds constituted the highest share among polycyclic aromatic hydrocarbons.

Keywords: polycyclic aromatic hydrocarbons, sewage sludge, compost

In Poland, application of composts and sewage sludge for fertilization is possible when these materials do not pose a threat connected with an excessive content of heavy metals or the presence of microorganisms and parasites [1, 2]. Currently, however, attention is drawn also to the presence of organic compounds belonging to persistent organic pollutants (POPs) in waste materials. Examples of POPs are: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and absorbable organic halides (AOX) [3-5]. They are compounds of anthropogenic origin which are carried for considerable distances (thereby occurring in places far away from where they originated). They are characterized by a long half-life period and lipophilic properties. These compounds show mutagenic, carcinogenic, teratogenic, and cytotoxic effects. What is important is that organic pollutants introduced into soils can be, similarly to trace elements, transferred to further links of the soil-plant-animal-human food chain, where they can be accumulated [6].

As it was highlighted above, POPs include, among others, polycyclic aromatic hydrocarbons. They are compounds which have between two and thirteen benzene rings arranged in linear, angle or cluster configurations. Number of rings in a PAH molecule determines compound properties - hydrocarbons with a greater number of rings are less volatile and less water-soluble, but more resistant to biological decomposition. It is

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[*] Contribution was presented during ECOpole'13 Conference, Jarnoltowek, 23-26.10.2013

confirmed by results of research by Banach-Szott et al [7]. The main anthropogenic sources of PAHs include: industry (petroleum refining), combustion of fossil fuels and waste, and road transportation (combustion of fuels as well as abrasion of tyres and asphalt) [3, 6]. Fertilization with PAH-containing materials derived from waste may increase the content of these compounds in soil and plants [8-10].

The research was conducted in order to determine the influence of fertilization with waste organic materials on the content of polycyclic aromatic hydrocarbons (PAHs) in soil. The following organic materials were analyzed for the impact they have: compost from green waste, municipal sewage sludge which was not composted, compost from sewage sludge and wheat straw as well as mixture of sewage sludge and hard coal ash.

Material and methods

Samples obtained in the third year of the field experiment were analyzed. The field experiment was carried out at the experimental station of the University of Agriculture, in Krakow-Mydlniki. The experiment was conducted on an acid soil (pH_{KCl} = 5.40) with grain-size distribution of light clay. Content of trace elements in the soil did not exceed the maximum permissible values established for agricultural use of sewage sludges, neither did the pH_{H2O} value of soil make fertilization with sewage sludge impossible [2]. The total content of 16 PAHs in the soil amounted to 488.3 $\mu g \cdot kg^{-1}$ d.m., whereas the soil contained:

- 17.5 $\mu g \cdot kg^{-1}$ d.m. of 2-ring PAHs,
- 88.8 $\mu g \cdot kg^{-1}$ d.m. of 3-ring PAHs,
- 243.8 $\mu g \cdot kg^{-1}$ d.m. of 4-ring PAHs,
- 138.2 $\mu g \cdot kg^{-1}$ d.m. of 5- and 6-ring PAHs.

The experiment was set up in 2008 and continued in the years 2009 and 2010. The field experiment comprised 7 fertilizing treatments (each conducted in 4 replications): non-fertilized soil (control treatment) as well as soil fertilized with mineral fertilizers, cattle manure, compost from green waste, stabilized municipal sewage sludge coming from a mechanical-biological sewage treatment plant, compost from municipal sewage sludge and wheat straw, and with a mixture of sewage sludge and hard coal ash.

Table 1

Content of PAHs in manure and organic materials used for fertilization

PAHs		Manure	Compost from green waste	Sewage sludge	Compost from sewage sludge and straw	Mixture of sewage sludge and ash
		[$\mu g \cdot kg^{-1}$ d.m.]				
Number of rings in a PAH molecule	2	478	28.3	1519	4589	7360
	3	37.7	128	2323	424	19,957
	4	n.s.*	911	680	3894	371
	5 + 6	n.s.	322	305	21.5	425
Sum of 16 PAHs		516	1389	4827	8929	28,113

* n.s. - not stated

Content of trace elements in the organic materials used for fertilization did not exceed the permissible value established for agricultural use of sewage sludges [2]. Among the materials used for fertilization, the lowest content of PAHs was found in manure, and the highest in mixture of sewage sludge and hard coal ash (Table 1). A high content of PAHs in the compost from green waste was due to the type of material used in composting - the compost was generated mainly from waste coming from maintenance of urban green areas.

The PR 39F58 maize of Pioneer was the test plant in all years of the research and it was grown for silage. In the 1st year of the experiment, the following doses of fertilization were used: 160 kg N, 168 kg P_2O_5, and 140 kg $K_2O \cdot ha^{-1}$. To the soil fertilized with manure and organic materials, the whole nitrogen dose was introduced in manure and those materials. Mineral fertilizers (ammonium nitrate, enriched superphosphate and potassium chloride) were used to introduce the nutrient elements to the soil in a treatment fertilized with mineral fertilizers and to equalize the doses of phosphorus and potassium in the soils of the remaining fertilized treatments. 100 kg N, 30 kg P_2O_5, and 110 kg $K_2O \cdot ha^{-1}$, all in the form of mineral fertilizers, were used in the 2nd and 3rd year of the research. Accurate data regarding conditions of conducting the experiment were included in the papers of Tabak and Filipek-Mazur [11, 12].

In the samples, the content of the following 16 compounds belonging to the group of polycyclic aromatic hydrocarbons, according to the list of the United States Environmental Protection Agency (US EPA), was determined: naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[g,h,i]perylene. The content of PAHs was determined using gas chromatograph with mass spectroscope Varian GC/MS/MS 4000, after solid phase extraction (SPE) using Bakerbond C18 500 mg/3 ml columns. FactorFour VF-5ms capillary column was used. Due to difficulty separating dibenzo[a,h]anthracene (5-ring compound) and indeno[1,2,3-cd]pyrene (6-ring compound), the content of 5- and 6-ring hydrocarbons was presented as a sum. The determination of the content of PAHs in each sample was conducted in two replications. In order to perform calibration, a method of comparison with an outside reference standard was used. Restek 610 PAH Calibration Mix A was chosen as reference standard.

Statistic elaboration of the results was made using Statistica 10 software. A univariate analysis of variance was carried out. Significance of differences between mean values was estimated using the Duncan test ($\alpha = 0.05$).

Results and discussion

After three years of the research, a significantly statistical influence of fertilization with manure, green waste compost and with sewage sludge on the content of 2-ring aromatic hydrocarbons in the soil was found (Table 2). Soil in treatments where the mentioned fertilization was introduced contained 93-141% more 2-ring aromatic hydrocarbons than the control soil. The content of 3- and 4-ring compounds in soil from two fertilized treatments was significantly lower than the content determined in the control soil - 61 and 40% in the soil fertilized with compost from sewage sludge and straw respectively, and 46 and 35% in the soil fertilized with manure. The soil fertilized with the mixture of sewage sludge and ash had 40% more 4-ring PAHs than the control soil, and the soil fertilized with green waste compost had 82% more PAHs. The soil fertilized with the mixture of sewage sludge and ash contained also 57% more 5- and 6-ring PAHs than the non-fertilized soil, and the soil fertilized with manure had 64% fewer of these PAHs.

The total content of the 16 PAHs in the soil of the experimental treatments was between 292 and 736 μg · kg^{-1} d.m. Compared with the control soil, the content of the sum of PAHs was lower by 43% in the soil fertilized with manure and by 42% in the soil fertilized with compost from sewage sludge and straw, and higher in the soil fertilized with green waste compost as well as with the mixture of sewage sludge and ash by 43 and 35% respectively. It was determined that the content of PAHs in the soil in two remaining treatments (fertilized with mineral fertilizers and sewage sludge) was close to the content found in the non-fertilized soil.

Table 2

Content of PAHs in soil

Treatment	**Number of rings in a PAH molecule**				**Sum of 16 PAHs**
	2	**3**	**4**	**5 + 6**	
	[μg · kg^{-1} d.m. ±SD]				
No fertilization	10.5a* ±1.0	98.3cd ±26.7	237.8b ±34.7	167.5bc ±57.0	514.1b ±19.6
Mineral fertilizers	11.6a ±1.5	114.9d ±27.7	245.5b ±10.9	166.7bc ±15.6	538.7b ±8.0
Manure	23.4b ±6.2	53.5ab ±24.3	155.0a ±46.8	60.5a ±18.2	292.4a ±28.0
Compost from green waste	20.3b ±3.9	100.2cd ±32.2	432.2d ±67.0	183.1c ±64.8	735.8d ±14.0
Sewage sludge	25.3b ±6.5	65.1abc ±2.3	295.6bc ±27.1	200.9cd ±15.4	586.9bc ±7.4
Compost from sewage sludge and straw	10.0a ±1.7	38.8a ±3.9	143.3a ±17.5	104.8ab ±26.3	296.9a ±14.9
Mixture of sewage sludge and ash	13.2a ±2.5	86.6bcd ±17.8	333.9c ±86.2	262.8d ±87.5	696.6cd ±23.5

* Mean values for parameter in columns marked with the same letters do not differ statistically significantly at $\alpha = 0.05$, according to the Duncan test

Soil in two treatments, one fertilized with green waste compost and one fertilized with the mixture of sewage sludge and ash (the content of the 16 PAHs was 736 and 697 μg · kg^{-1} d.m. respectively), was polluted with hydrocarbons. According to criteria proposed by the Institute of Soil Science and Plant Cultivation [6], the pollution was small (II degree). It is not recommended to cultivate special crops designated for the production of food with few harmful substances on such polluted soils.

The content of PAHs in the soil determined in own research did not differ from the literature data. In Poland in 2010, in soils of agricultural use, the mean content of 13 PAHs (according to the US EPA list, without naphthalene, acenaphthylene and acenaphthene) amounted to 558 μg · kg^{-1} d.m. (data for 216 measuring points), whereas in the Malopolska province the content of 13 PAHs was between 122 and 4903 μg · kg^{-1} d.m. (data for 17 measuring points) [12]. In the measuring point located in Krakow, where the field experiment was conducted, the content of 13 PAHs amounted to 1920 μg · kg^{-1} d.m. in 2010, whereas in soils collected from two points located in villages closest to the research site the content of 13 PAHs was 393 and 644 μg · kg^{-1} d.m. [13]. In own research, the total content of 13 PAHs in soil was between 267 and 710 μg · kg^{-1} d.m.

4-ring compounds constituted the highest share among polycyclic aromatic hydrocarbons determined in the soil (Fig. 1). They constituted between 46 and 59% of all determined PAHs.

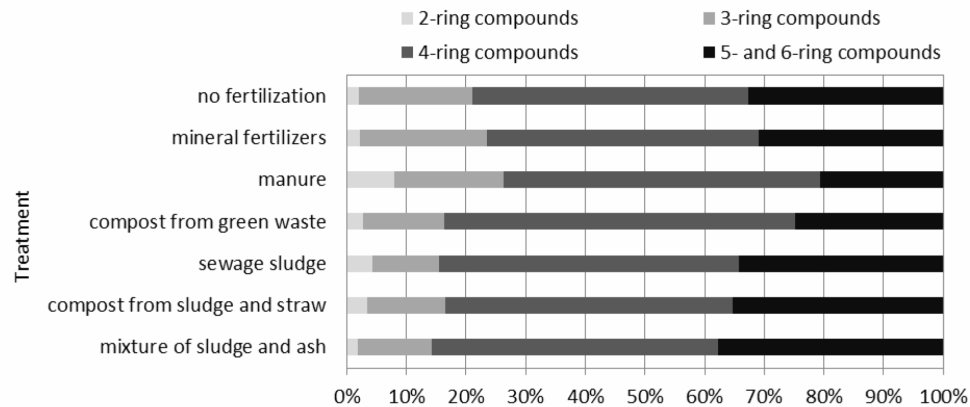

Fig. 1. Share of PAHs with different numbers of rings in sum of 16 PAHs

Conclusions

The carried out research revealed that the mixture of sewage sludge and ash (*ie* material containing the highest amount of polycyclic aromatic hydrocarbons) as well as the compost from green waste had an unbenefical effect on the content of PAHs in the soil. Particularly, fertilization with the compost from sewage sludge and straw did not pose a threat of soil pollution with polycyclic aromatic hydrocarbons.

Acknowledgements

The research results carried out within the subject No. 3101 were financed from the subsidy for science granted by the Polish Ministry of Science and Higher Education.

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Abstrakt: Celem badań było określenie wpływu nawożenia odpadowymi materiałami organicznymi na zawartość wielopierścieniowych węglowodorów aromatycznych (WWA) w glebie. Analizom poddano próbki uzyskane w trzecim roku doświadczenia polowego obejmującego 7 obiektów: glebę nienawożoną oraz nawożoną nawozami mineralnymi, obornikiem bydlęcym, kompostem z odpadów zielonych, osadem ściekowym, kompostem z osadu ściekowego i słomy pszennej oraz mieszaniną osadu ściekowego i popiołu z węgla kamiennego. Rośliną testową była kukurydza uprawiana na kiszonkę. Zawartość 16 związków z grupy wielopierścieniowych węglowodorów aromatycznych (według listy Amerykańskiej Agencji Ochrony Środowiska) w glebie oznaczono techniką chromatografii gazowej z detekcją masową po ekstrakcji do fazy stałej. Gleba nawożona obornikiem i kompostem z osadu ściekowego i słomy charakteryzowała się mniejszą łączną zawartością 16 WWA od gleby kontrolnej, natomiast gleba nawożona kompostem z odpadów zielonych oraz mieszaniną osadu ściekowego i popiołu - zawartością większą. W glebie pozostałych dwóch obiektów oznaczono zawartość WWA zbliżoną do stwierdzonej w glebie nienawożonej. Wśród wielopierścieniowych węglowodorów aromatycznych największy udział stanowiły związki 4-pierścieniowe.

Słowa kluczowe: wielopierścieniowe węglowodory aromatyczne, osad ściekowy, kompost