

THE INFLUENCE OF THE DOSES OF WASTE ACTIVATED SLUDGE ON THE CONTENT OF PAHs IN THE RYEGRASS AND SOIL

STANISŁAW KALEMBASA¹, BEATA WIŚNIEWSKA¹, MARIUSZ KLUSKA²

¹Academy of Podlasie, Soil Science and Plant Nutrition Department, ul. Prusa 14, 08-114 Siedlce, Poland

²Academy of Podlasie, Department of Chemistry and Environmental Protection, ul. 3. Maja 54, 08-114 Siedlce, Poland

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WPLYW DAWKI OSADU ŚCIEKOWEGO NA ZAWARTOŚĆ WWA W ŻYCICY WIELOKWIATOWEJ I UTWORZE GLEBOWYM

Zawartość wielopierścieniowych węglowodorów aromatycznych w plonie suchej masy życicy wielokwiatowej uzależniona była od dawki osadu ściekowego. Największą ilość sumy oznaczonych węglowodorów w plonie trawy stwierdzono na obiekcie kontrolnym. Na obiektach nawożonych osadem ściekowym najwięcej węglowodorów zanotowano w życicy wielokwiatowej uprawianej na piasku gliniastym lekkim pylastym z 20% udziałem osadu. Po dwóch latach prowadzenia doświadczenia największą sumaryczną ilość węglowodorów stwierdzono na obiekcie kontrolnym. W utworze glebowym gdzie stosowano osad ściekowy ilość WWA wzrasta wraz ze wzrostem dawki osadu.

Summary

The concentration of hydrocarbons in the yield of dry matter in ryegrass depended upon the sludge dose. The highest concentrations of hydrocarbons in ryegrass were found in a control object. In objects fertilized with waste activated sludge the highest concentration of hydrocarbons was found in ryegrass with 20% of waste activated sludge. After a two-year experiment, the highest concentration of hydrocarbons was found in the control object. In soil materials fertilized with waste activated sludge the concentration of hydrocarbons grew along with the sludge dose.

INTRODUCTION

In the last years a considerable increase of interest in pollution of environmental by natural organic compounds such as polycyclic hydrocarbons has been noticed.

These compounds are normally produced during the burning processes and exist in all elements of natural environment. A lot of PAHs accumulate in soils mainly by the application of composts, waste activated sludge as well as with dust and atmospheric precipitation [6, 8, 10].

The PAHs have toxic, genotoxic, mutagenic, and carcinogenic properties [2, 7]. Due to the fact the PAHs are relatively stable compounds in the environment; they are very often called stable organic impurities [14, 18].

Apart from high stability of these compounds a big proportion of them are removed from the soil environment as the result of biological or chemical decomposition, leaching or evaporation. The cultivation of vegetables on the soils with high concentration of PAHs weathers the danger of their uptake by plants and, furthermore, their introduction

into the nutritional chain [9, 16]. From the results of the influence of the root system of plants on the PAHs in soils reported by Aprill and Sims [1], Morel et al [11] Reilly et al [13], Siuta [15] it appears that at the beginning of vegetation period plants stimulated the decomposition process of PAHs while at the prolongation period the influence of plant was weaker. In this investigation the grasses were used as the tested plants.

The determination of the influence of various doses of waste activated sludge on the concentration of PAHs in ryegrass and soil was the aim of this investigation.

MATERIALS AND METHODS

This investigation was carried out in a pot experiment in the glasshouse and in the second year after the application of waste activated sludge. The experiment was layed out in comple of leaseive soil which belongs to the typical brown type and is classified as autogenic soil.

The pots were filled with 10 kg of soil material and the following scheme of the experiment was designed:

1. control object (only soil materials);
2. soil material + 10% (w/w) of cattle farmyard manure (standard object);
3. soil material + 10% (w/w) of waste activated sludge;
4. soil material + 20% (w/w) of waste activated sludge;
5. soil material + 30% (w/w) of waste activated sludge.

The farmyard manure used in this experiment was collected from milk cows, and waste activated sludge was produced on the sewage purification plants at Siedlce. The tested plant was ryegrass (*L. multiflorum* Lam.) which was cut four times in the intervals of 30 days. The results presented in this paper were obtained in the second year of experiment i.e. in the second year of cultivation of ryegrass after farmyard manure and waste activated sludge were applied as the fertilizers.

The samples of ryegrass after each cut were air dried, ground and in so prepared material PAHs were determined. Soil samples from the whole volume of soil material were taken from each pot after the fourth cut and like plant materials were ground and sieved through the sieve with 0.25 mm of diameter.

The PAHs from plant and soil samples were extracted in the Soxhlet apparatus for 8 hrs with hexane and after the concentration on the vacuum evaporator were purified on the PAH Soil art. no. 7518-08 column (having 500 mg of stable phase Cyjano/1000 mg of silica gel). The PAHs from the column were washed out with the mixture of the acetonitrile with toluene at the ratio 3:1, and the eluat was evaporated to dryness and the dry residue was dissolved in 2 cm³ of acetonitrile and injected on the top of column HPLC (Backerbond) PAH 16 plus art. nr 7504-00.

The concentrations of PAHs were determined by HPLC method.

RESULTS AND DISCUSSION

The content $\mu\text{g}/\text{kg}$ of DM of determined PAHs was differentiated in farmyard manure and waste activated sludge applicated to the soil material in this experiment (Tab. 1). In the farmyard manure the acenaphthalene was determined in the biggest amount 892 $\mu\text{g}/\text{kg}$ whereas the concentration of phenanthrene was 0.346 $\mu\text{g}/\text{kg}$.

Table 1. The content ($\mu\text{g}/\text{kg}$ of DM) of PAHs in FYM and waste activated sludge applied in pot experiment

PAHs	FYM	Waste activated sludge
Naphthalene	229	73.2
Acenaphthalene	892	357
Acenaphthene	–	0.789
Fluorene	–	–
Phenanthrene	0.346	0.0252
Fluoranthene	–	6.79
Pyrene	1.82	–
Benzo(a)pyrene	–	0.630
Dibenzo(a,h)anthracene	–	0.0438
Sum	1123.2	438.5

Among the analyzed PAHs in farmyard only 4 of them were found and their sum reached $1123.2 \mu\text{g}/\text{kg}$ of DM.

In the waste activated sludge the total concentration of all determined PAHs reached $438.5 \mu\text{g}/\text{kg}$ of DM and this figure of PAHs was stated [5]. The yield of dry mass of ryegrass (Tab. 2) was significantly differentiated under the influence of the application of the doses of waste activated sludge and farmyard manure. It was probably caused by different doses of nitrogen which had been introduced with organic fertilizers and was as follows: with farmyard manure $4.0 \text{ g}/\text{pot}$ and with the doses 10, 20 and 30% of waste activated sludge 9.5 ; 19.0 and $28.5 \text{ g}/\text{pot}$, respectively. This relationship between the yield of plants and doses of waste activated sludge is often reported by authors [12, 17].

Table 2. The yield (g/pot of DM) of ryegrass in the second year of experiment

Cuts	Fertilization					Means
	Control	FYM 10%	WAS* 10%	WAS* 20%	WAS* 30%	
I	6.8	13.9	13.1	18.6	16.6	13.8
II	10.4	11.5	11.2	10.5	7.1	10.1
III	5.7	8.4	8.1	10.4	8.5	8.2
IV	4.3	5.1	4.9	6.3	4.1	4.9
Sum	27.2	38.9	37.3	45.8	36.3	37.1

* WAS – waste activated sludge

LSD_{0.05} for fertilization – 5.67

LSD_{0.05} for fertilization – 6.90

The concentration ($\mu\text{g}/\text{kg}$) of determined PAHs as the sums for all 4 cuts was very much differentiated upon the investigated PAHs and the objects of fertilization (Tab. 3). The naphthalene was found in the biggest concentration and reached up to $34.0 \mu\text{g}/\text{kg}$ of DM. Among all the determined PAHs five (naphthalene, acenaphthalene, acenaphthene, fluorene and benzo(k)fluoranthene) exceeded the concentration of $1.0 \mu\text{g}/\text{kg}$ and the sums of those reached 87.4 up to 97.5% of the total sum of all PAHs taken as 100% . Naphthalene was the one of all whose concentration was the biggest as a mean for all fertilization objects that reached $34 \mu\text{g}/\text{kg}$ of DM and ranged from $21 \mu\text{g}/\text{kg}$ on the object with 10% addition of waste activated sludge up to $49.0 \mu\text{g}/\text{kg}$ of DM in the ryegrass harvested from

the control object. The benzo(k)fluoranthene was found in the ryegrass harvested from all objects, but the content of this PAHs was not high and reached 3.18 $\mu\text{g}/\text{kg}$ of DM. Similar results have been reported by Edwards [3, 4] and Sims and Overcash [14].

Table 3. The content ($\mu\text{g}/\text{kg}$ of DM) of the PAHs in the ryegrass

No.	Determined PHCs	Soil material					
		Control	10% FYM	10% WAS	20% WAS	30% WAS	Mean
		Sum of cuts					
1	Naphthalene	49.0	23.0	21.0	43.0	34.0	34.0
2	Acenaphthalene	6.5	5.3	3.0	3.8	0.9	3.90
3	Acenaphthene	1.0	3.0	8.0	4.2	8.4	4.92
4	Fluorene	8.7	12.0	10.0	7.0	6.0	8.74
5	Phenanthrene	0.5	0.3	0.4	0.3	0.2	
6	Anthracene	0.02	0.17	4.3	0.17	0.21	
7	Fluoranthene	0.76	0.45	0.83	0.63	0.68	
8	Pyrene	0.27	0.29	0.36	0.39	0.067	
9	Benzo(a)anthracene	0.27	0.33	0.04	–	0.37	
10	Chrysene	–	–	0.06	0.68	–	
11	Benzo(b)fluoranthene	–	–	0.05	0.02	–	
12	Benzo(k)fluoranthene	3.1	5.69	1.7	2.8	2.6	3.18
13	Benzo(a)pyrene	–	–	0.41	–	–	
14	Dibenzo(a,h)anthracene	–	–	0.22	1.5	0.18	
Sum 1–14		70.0	51.0	50.0	64.0	54.0	
Sum 1–5		68.3	48.9	43.7	60.8	51.9	
% of the sums 1–5 inside the sum of 1–14		97.5	96.0	87.4	95.0	96.1	

The content ($\mu\text{g}/\text{kg}$ of DM) of PAHs in soil samples taken from pots after fourth cut of ryegrass was not in so high concentration as in plant samples (Tab. 4). The biggest amount 2.82 $\mu\text{g}/\text{kg}$ among all PAHs was the naphthalene similarly to plant samples. The application 10% of FYM and waste activated sludge caused decrease in the concentration of determinate PAHs in grass and soil material what probably was caused by high activity of microorganisms. The application of high doses of waste activated sludge might have increased the concentration and cumulating of PAHs in soils.

On the basis of the concentration of PAHs in the plant and soil samples the correlation coefficient was calculated and the value reached $r = +0.74^{**}$, $\alpha = 0.01$, $Y = 7.08 + 5.57 x$. So high and significant value of the correlation coefficient may suggest that part of PAHs formed in soil during the decomposition process of waste can be uptake by plants.

Table 4. The content ($\mu\text{g}/\text{kg}$ of DM) of the PAHs determined in the soil samples taken after 4 cuts of ryegrass

No.	Determined PHCs	Soil material					
		Control	10% FYM	10% WAS	20% WAS	30% WAS	Mean
		Sum of cuts					
1	Naphthalene	8.4	1.2	0.75	0.63	3.1	2.82
2	Acenaphthalene	0.19	0.27	0.38	0.37	0.31	0.30
3	Acenaphthene	–	0.048	0.15	0.09	0.13	–
4	Fluorene	0.72	0.84	1.3	1.0	0.93	0.96
5	Phenanthrene	0.014	0.011	0.054	0.032	0.044	
6	Anthracene	–	0.029	–	0.014	–	
7	Fluoranthene	0.095	–	–	–	–	
8	Pyrene	0.028	0.011	0.022	0.062	0.015	
9	Benzo(a)anthracene	0.051	–	–	0.002	0.08	
10	Chrysene	–	–	–	–	–	
11	Benzo(b)fluoranthene	0.0006	–	–	0.02	0.033	
12	Benzo(k)fluoranthene	0.04	0.018	0.009	0.01	0.008	
13	Benzo(a)pyrene	0.15	–	–	–	–	
14	Dibenzo(a,h)anthracene	–	–	–	–	–	
Sum 1–14		10.0	2.36	3.0	3.5	5.0	
Sum 1 + 2 + 4		9.31	2.31	2.43	2.0	4.34	
% of the sums 1 + 2 + 4 in the sum of 1–14		93.1	97.8				

CONCLUSIONS

1. The yield of ryegrass dry matter was significantly differentiated upon the influence of the applied organic fertilizer as well as among the cuts.
2. The higher amount of PAHs (sums of all determined PAHs) was found in ryegrass harvested from the control object and the lowest in the objects with the sludge applied in the dose of 10%.
3. In the soil after two years of the mineralization of organic fertilizers the biggest cumulating of all determinates PAHs was stated in the control object and on the object with waste activated sludge the concentration of PAHs was parallel with the dose of this waste.

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