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Degradation of polycyclic aromatic hydrocarbons in soil with sewage sludges

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ABSTRACT

Many publications point out to sewage sludge as a significant sources of polycyclic aromatic hydrocarbons (PAH). Some authors note that the amount of PAHs in plants increases as their concentration in the soil increases. It was often believed that as they are high-molecular compounds, their ability to migrate to plants is limited. In their studies, the authors of the present work took note of the contents of PAHs in sewage sludges used for agricultural purposes. They were used to fertilize a sandy soil in a dose of 10, 50, 100 and 200 t/ha, respectively. The tests were conducted in pot cultures under natural conditions. Osier willow (salix) and dactylis were grown on the sludge-soil mixtures. The use of sewage sludges for fertilization caused a significant increase in the contents of polycyclic aromatic hydrocarbons in the soils. The application of manure for fertilization resulted in the lowest increase in the contents of these components in the fertilized grounds. It was also found that fertilization with manure did not cause any significant increase in PAH contents in the plants grown. No increase in PAH contents in plants with increasing manure dose was noted either.

Keywords: Sewage sludge; Manure; Fertilizer; Soil; Plant; PAH

1. Introduction

Wastewater treatment is accompanied by generation of sewage sludge which is commonly referred to as organic and mineral solid phase. The primary goal of sewage sludge utilization is mineralization of organic matter. Sewage sludge is generated at different stages of the wastewater treatment process. The quantity of generated sewage sludge depends on origin, composition, organic matter content, the decay rate during stabilization, and the dehydration degree [1,2].

Sewage sludge contains significant quantities of organic matter and is a source of nutrients essential for plants, and therefore its fertilizing value is much higher than manure or liquid manure commonly applied in agriculture. However, the main barrier which prevents from using sewage sludge as a fertilizer in agriculture is the excessive content of heavy metals, polycyclic aromatic hydrocarbons and sanitary contaminations [3–7].

Polycyclic aromatic hydrocarbons constitute a group of compounds which present serious environmental threats with the rapid development of conversion processes. They comprise approximately 200 out of 800 well-known carcinogenic compounds. PAHs constitute severe health risk for human beings and animals as introduced into the system are metabolized and form mutagenic and carcinogenic derivatives. The most hazardous are: naphthalene, acenaphthene, acenaphthylene, fluorene, phenantrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene. The severe toxicity of PAHs is caused by their mutagenic, genotoxic and carcinogenic properties which disclose even when these compounds are present in trace quantities. Polycyclic

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aromatic hydrocarbons are introduced to soil through atmospheric contaminations, sewage sludge and sewage sludge-based composts which are used in agriculture [8,9]. The presence of PAHs in soils impairs the biological equilibrium. Toxic effects of polycyclic aromatic hydrocarbons depend on the concentration and time of action towards soil microorganisms.

Polycyclic aromatic hydrocarbons show strong sorption affinity to soils. They do not dissolve in water easily and are relatively resistant to biological and chemical decomposition. It has been confirmed that PAHs can accumulate in living organisms, and also can cause synergetic mechanisms with other contaminants, e.g. heavy metals [10,11].

2. Materials and methods

The concentration of chemical compounds in sewage sludge is changeable and usually depends on type and composition. When introduced to soils in uncontrolled manner sewage sludge may cause irreversible changes in soil composition. Chemical contaminants which easily migrate in the environment are accumulated in soils and plants during vegetation. They can also destroy biological activity of soil [12,13]. The authors of the presented study investigated the problem of accumulation of PAHs in sewage sludge, soils fertilized with sewage sludge and plants grown on these substrates. Natural fertilizer, i.e. manure was used for the comparison. Sandy soil was used for the investigations. Prior to the investigations, pH of selected soil was measured potentiometically and was about 5.5. Sewage sludge was sampled from the following wastewater treatment plants: Pajęczno, Rokitnica and Koluszki (untreated and treated with a polyelectrolyte). Also straw-bedded cattle manure was used for the comparison.

Sewage sludge sampled from the Pajeczno wastewater treatment plant was stabilized aerobically, thickened mechanically and dewatered on the belt press. The characteristics of sewage sludge included greasy consistence and unpleasant odor.

Sewage sludge sampled from the Rokitnica wastewater treatment plant was generated during biological wastewater treatment. Sewage sludge was dewatered gravitationally in lagoons located by the plant. The consistence of this sludge was somewhat clayey, the odor was perceptible but not bothersome.

Sewage sludge sampled from the Koluszki wastewater treatment plant was generated during biological treatment of wastewater (untreated and treated with polyelectrolyte samples). Both types of sewage sludge were characterized by unpleasant odor. However, the consistence of these samples was different: untreated sewage sludge was liquid and sewage sludge treated with polyelectrolyte was somewhat greasy (was dewatered before use).

The manure used for the investigations was sampled from a cattle farm.

The vase-life experiments were performed on the laboratory scale. The experiments were conducted in 10 L vases in 3 replications. The sandy soil was fertilized with the investigated fertilizers in the following ratios (based on 10 kg of sandy soil): 10, 50, 100, 200 t/ha of sewage sludge and manure, respectively (on a dry basis).

For graphical description of the experiments the following abbreviations were used:

- P – soil fertilized with sewage sludge sampled from the Pajeczno wastewater treatment plant,
- R – soil fertilized with sewage sludge sampled from the Rokitnica wastewater treatment plant,
- Kbp – soil fertilized with untreated sewage sludge sampled from the Koluszki wastewater treatment plant,
- K – soil fertilized with sewage sludge treated with a polyelectrolyte sampled from the Koluszki wastewater treatment plant,
- O – soil fertilized with the manure.

The prepared mixtures of soil and selected fertilizers in different ratios were used for cultivation of Salix viminalis and Orchard grass (*Dactylis glomerata*). The experiment started in 2006 and lasted for the entire vegetation season. After completion of the experiment (a year after fertilization), soil samples were taken for the analysis. The concentration of PAHs in sewage sludge and manure before the start of the experiment as well as in soil mixtures with sewage sludge and manure, and the plants was determined by chromatography.

3. Results and discussion

The concentrations of PAHs in the sewage sludge and manure used as fertilizers are presented in Table 1.

According to the Polish standards [14] on the municipal sewage sludge and its potential for further applications (e.g. in agriculture), the determination of polycyclic aromatic hydrocarbons is not required. However, according to the EU and U.S. Environmental Agency (U.S. EPA) recommendations, the determination of 16 the most hazardous PAHs is obligatory. The determination of PAHs in sewage sludge has become a relevant topic in Europe since the 3rd draft directive of the European Union released regulation on the total PAHs values allowed in sewage sludge used for agriculture (6000 ng g^{-1} calculated as the sum of acenaphthene, phenanthrene, fluorene, fluoranthene, pyrene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene and indeno [1,2,3-cd]pyrene), but it is not allowed concentration higher than 1000 ng g^{-1} for benzo[a]pyrene [10].

In this paper, the authors studied the temporal evolution of the 16 PAHs listed in the U.S. EPA priority

Table 1
The concentrations of polycyclic aromatic hydrocarbons in the investigated sewage sludge, manure and sandy soil (control)

No.	Polycyclic aromatic hydrocarbon (μg/kg d.m)	Sewage sludge sampled from the following water treatment plants				Manure	Control
		Pajeczno	Rokitnica	Koluszki	Kolusz.bp		
1	Naphthalene	1040	1350	2700	6800	11	5.9
2	Acenaphthylen	86	69	90	69	90	4
3	Acenaphtene	100	118	223	215	4.8	0.2
4	Fluorene	22	179	581	472	11	0.3
5	Phenantrene	672	963	794	763	96	1.4
6	Anthracene	114	93	45	75	17	0.2
7	Fluoranthene	1080	1060	1230	1070	77	0.9
8	Pyrene	759	766	872	769	45	0.8
9	Benzo(a)anthracene	607	515	398	275	22	0.2
10	Chrysene	1270	472	508	501	31	0.4
11	Benzo(b)fluoranthene	1070	441	430	415	28	0.4
12	Benzo(k)fluoranthene	470	220	230	194	13	0.2
13	Benzo(a)pyrene	718	344	338	301	19	0.3
14	Dibenzo(a,h)anthracene	219	84	68	51	4.8	0.2
15	Benzo(g,h,i)perylene	660	347	342	257	15	0.7
16	Indeno(1,2,3-c,d)pyrene	820	263	254	294	20	0.2

list. These 16 PAHs are: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a] anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a] pyrene, dibenzo[a,h]anthracene, benzo- [g,h,i]perylene and indeno[1,2,3-cd]pyrene.

In view of the recommended standards and according to the data presented in Table 1, the investigated sewage sludge contained excessive quantities of PAHs. In case of manure the concentration of PAHs met the recommended standards. However, with reference to the Polish standards on the sanitary requirements and the content of heavy metals (data presented elsewhere), the investigated sewage sludge could be used in agriculture. Generally, the addition of sewage sludge to soil alters chemical and biological composition of soil [2,11,12]. The investigated sewage sludge and manure used as fertilizers caused the change in soil parameters. The addition of sewage sludge resulted in a significant increase in PAHs in the soils subjected to fertilization. We present the concentration of PAHs in fertilized soils in Figs. 1 and 2 (due to limited space we selected the most hazardous hydrocarbons, i.e. pyrene and benzo(a)pyrene).

Of particular importance for the transformations and accumulation of various compounds (e.g. heavy metals and PAHs) in soils is the reaction of the ground. The testing results for the pH of fertilized soils are summarized in Fig. 1.

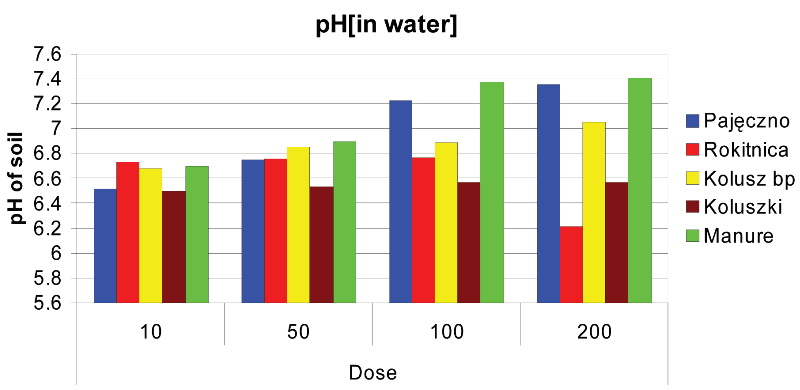

Fig. 1. Reaction of sandy ground as fertilized with different doses of sewage sludge and manure.

Manure increased the ground reaction in all samples and application doses. Sewage sludges behaved less stably in that environment. Some of them acidified the soil. That was the case for the Rokitnica sewage sludge, whereas the Pajęczno sewage sludge alkalized the soil reaction. In his investigation into the quantitative changes of PAHs during sewage sludge composting, Oleszczuk [9] observed a decline in the PAH amount with increasing sewage sludge pH.

The selected 16 PAHs are particularly hazardous, with benzo(a)pyrene being ranked first. These compounds exhibit a relatively low acute toxicity, but a very distinct chronic toxicity. The human body assimilates 3–4 mg PAHs, while their permissible water concentration is 0.2 mg/dm^3. These are very dangerous compounds, as they provoke cancerous lesions in various tissues. Sewage sludge introduced to soil may contribute to the contamination with polycyclic hydrocarbons of both the fertilized ground and the biomass obtained. Most of those compounds undergo biodegradation, however their presence might disturb the biological balance. The best investigated hydrocarbon of the PAH group is benzo(a) pyrene that, due to its carcinogenic power and widespread occurrence in the environment, is recognized as the indicator for the entire PAH group [10]. Its content of sewage sludge to be utilized in agriculture may not be higher than 1000 ng g^{-1}. In the sewage sludges tested, this value was not exceeded. However, the Pajęczno sewage sludge contained a relatively high content of benzo(a) pyrene. The manure used for the tests contained a negligible amount of this compound.

The values of the relative carcinogenesis factors for 9 particularly dangerous PAHs in the environment are as follows:

Dibenzo(a,h)anthracene	5
Benzo(a)pyrene	1
Benzo(a)anthracene	0.1
Benzo(b)fluoranthene	0.1
Benzo(k)fluoranthene	0.1
Indeno(1,2,3-c,d)pyrene	0.1
Anthracene	0.01
Chrysene	0.01
Benzo(g,h,i)perylene	0.01

The contents of these 9 selected compounds in the soils fertilized with, respectively, sewage sludge and manure (two series S1 and S2) are shown in Figs. 2–10.

When analyzing the data on the PAH contents in fertilized soils, an tendency of these pollutants to increase with increasing fertilizer dose is found. Similar results were also obtained by Cai et al. [15].

The content of pyrene and benzo(a)pyrene (regarded as particularly dangerous for the environment) in the fertilized soils increased after sewage sludge application.

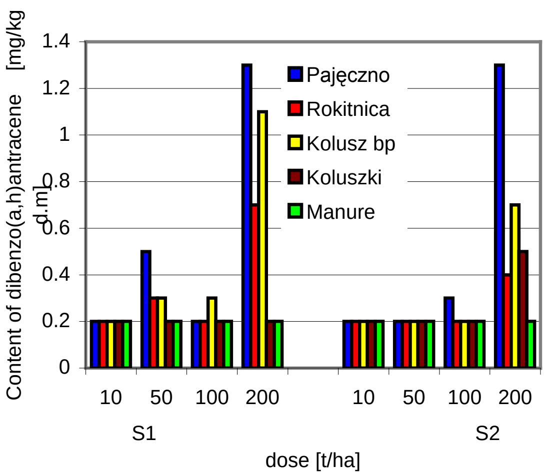

Fig. 2. Content of dibenzo(a,h)anthracene.

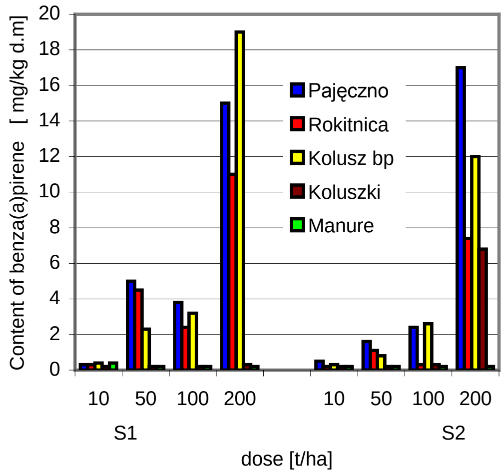

Fig. 3. Content of benzo(a)pyrene.

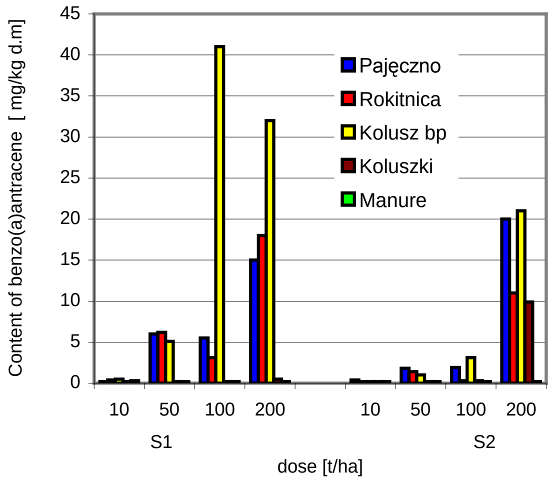

Fig. 4. Content of benzo(a)anthracene.

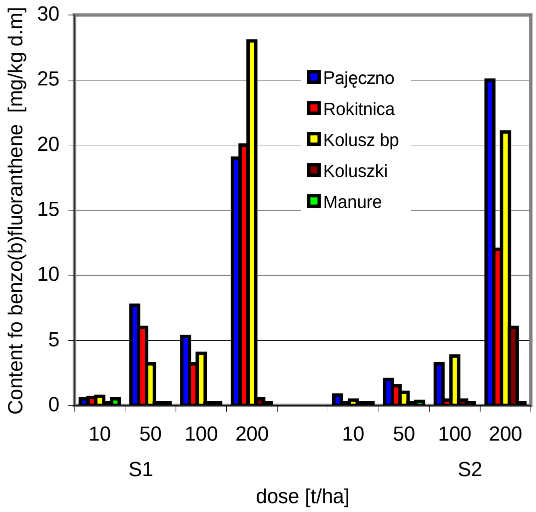

Fig. 5. Content of benzo(b)fluoranthene.

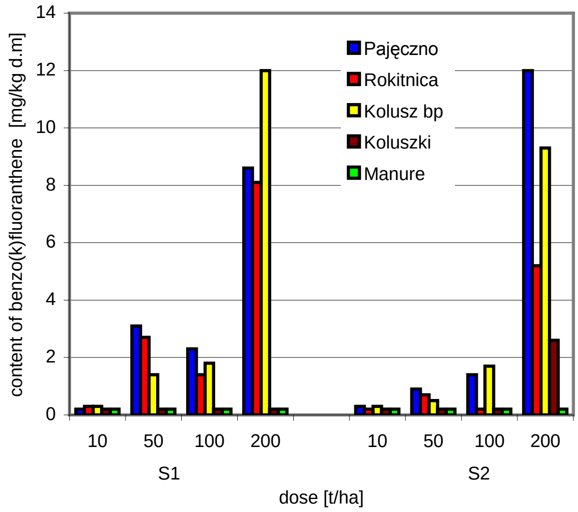

Fig. 6. Content of benzo(k)fluoranthene.

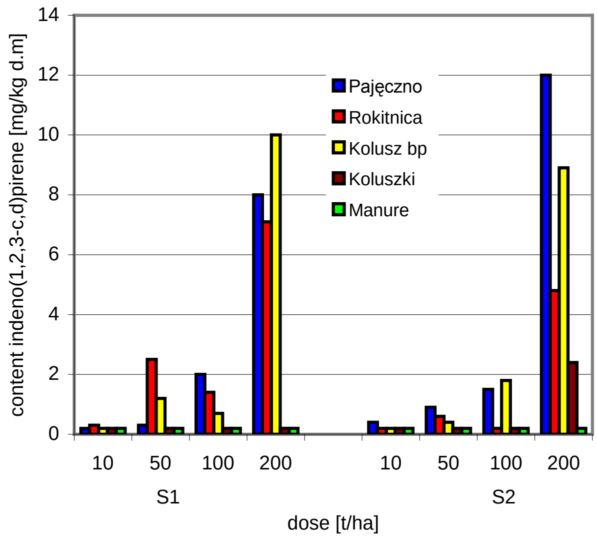

Fig. 7. Content of indeno(1,2,3-c,d)pyrene.

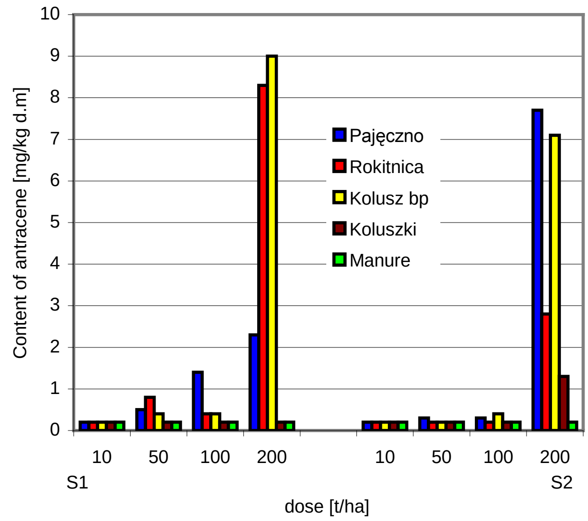

Fig. 8. Content of anthracene.

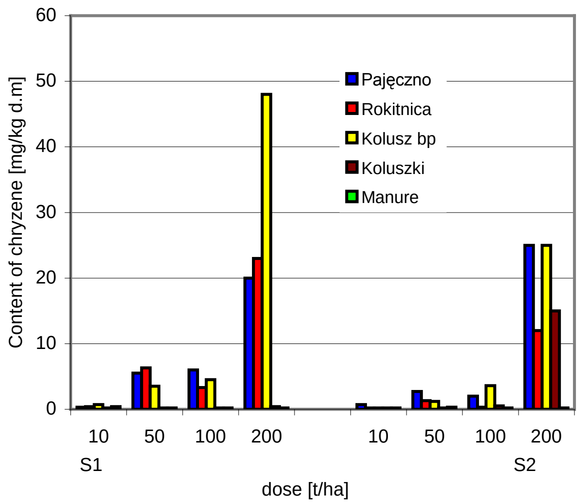

Fig. 9. Content of chrysene.

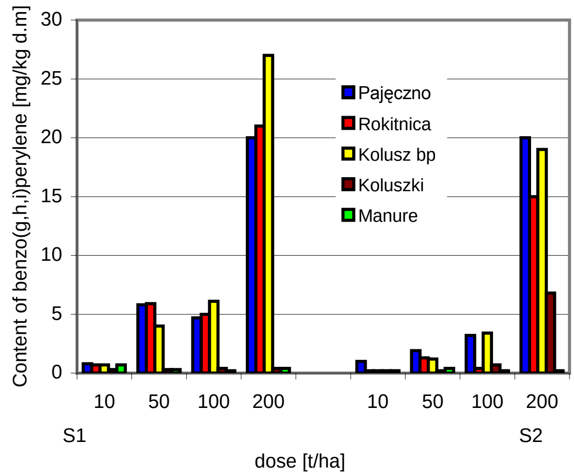

Fig. 10. Content of benzo(g,h,i)perylene.

Polycyclic aromatic hydrocarbons are believed to be little mobile in the environment and strongly bonded with an organic substance [1]. Publications on this problem often point out to a low hazard resulting from the contamination with PAH of vegetation growing on soils rich in these compounds. Nevertheless, the authors draw attention to the fact that thus grown biomass being threatened with PAH bioaccumulation is real and might pose a problem to the health of humans and animals [15].

Table 2 shows the results of examination of PAH contents in plants originating from soils fertilized with sewage sludge and manure, respectively. In the present paper, only the results concerning the soils treated with the Koluszki sewage sludge are used (because it is these grounds that the plants grew best and did not die, which was the case with soils treated with other sewage sludges).

When analyzing the data in Table 2 it can be found that the fertilization with manure has not caused any significant increase in PAH contents in plants grown. No increase in the contents of these compounds in plants with increasing manure dose has been noted, either. Whereas, in plants harvested from soils fertilized with sewage sludge, a distinct influence of increasing sewage sludge doses on the increase in PAH contents has been found.

4. Conclusions

All sewage sludges used for the tests were, according to Polish standards, suitable for natural (or even agricultural) utilization. However, the contents of PAHs assayed in those sewage sludges exceeded the European Union standards. The use of sewage sludges for fertilization caused a significant increase in the contents of polycyclic aromatic hydrocarbons in the soils. The observations made are in agreement with the investigation results reported in work [10]. The application of manure for fertilization resulted in the lowest increase in the contents of these components in the fertilized grounds.

It was also found that fertilization with manure did not cause any significant increase in PAH contents in the plants grown. No increase in PAH contents in plants with increasing manure dose was noted, either. Whereas, in plants harvested from soils fertilized with sewage sludge, a distinct influence of increasing sewage sludge doses on the increase in PAH contents was found.

Similar results were obtained by Cai et al. [15], who analyzed the overall (total) PAH content in the roots of Raphanus dativus in their investigation. The above-mentioned plant was grown on soils fertilized with compost prepared from sewage sludge. The authors of the quoted work found a positive correlation between the contents of PAHs accumulated in roots and the sewage sludge compost dose applied. The authors drew also attention to a possible transfer of PAHs from the soil to the roots and then to the sprouts of plants.

Acknowledgment

The investigations results and the present publica-

Table 2
Results of the examination of PAH contents in plants originating from grounds fertilized with sewage sludge (derived from the Koluszki sewage treatment plant)

Lp	Assay (μg/kg d.m)	Koluszki D = 10		Koluszki D = 50		Koluszki D = 100		Koluszki D = 200		Control
1	Naphthalene	86	(34)	96	(14)	135	(39)	136	(28)	30
2	Acenaphthylen	43	(<15)	42	(23)	43	(23)	66	(21)	<18
3	Acenaphtene	2.5	(3.3)	2.5	(<1.1)	7.2	(1.4)	12	(<1.0)	1.0
4	Fluorene	7.3	(12)	6.4	(3.3)	8.3	(6.1)	20	(3.7)	5.4
5	Phenantrene	54	(97)	49	(26)	83	(45)	120	(23)	25
6	Anthracene	2.4	(3.2)	<2.0	(<1.1)	<2.0	(1.4)	3.9	(1.0)	1.0
7	Fluoranthene	28	(12)	24	(3.1)	38	(15)	74	(7.3)	5.2
8	Pyrene	37	(11)	28	(2.8)	53	(21)	107	(7.3)	4.1
9	Benzo(a)anthracene	<2.3	(<0.8)	<2.3	(<1.2)	<2.3	(<1.2)	<3.5	(<1.1)	<0.9
10	Chrysene	3.9	(3.9)	3.4	(<1.2)	8.2	(3.6)	14	(1.2)	1.3
11	Benzo(b)fluoranthene	4.8	(1.3)	4.5	(<1.1)	7.9	(1.3)	11	(<1.0)	0.8
12	Benzo(k)fluoranthene	2.2	(<0.6)	1.9)	(<0.9	3.4	(<0.9)	4.1	(<0.8)	<0.7
13	Benzo(a)pyrene	2.9	(<0.7)	<2.0	(<1.1)	5.1	(<1.1)	7.0	(<1.0)	<0.8
14	Dibenzo(a,h)anthracene	<2.3	(<0.8)	<2.3	(<1.2)	<2.3	(<1.2)	<3.5	(<1.1)	<0.9
15	Benzo(g,h,i)perylene	4.0	(<0.8)	<2.3	(<1.2)	5.1	(<1.2)	6.2	(<1.1)	<0.9
16	Indeno(1,2,3-c,d)pyrene	2.4	(<0.7)	<2.0	(<1.1)	3.8	(<1.1)	3.8	(<1.0)	<0.8

(*) For comparison, PAH contents in plants harvested from soils fertilized with manure are given in parentheses.

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