# Content of polycyclic aromatic hydrocarbons in soils polluted with petrol and diesel oil after remediation with plants and various substances

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### ABSTRACT

The study was undertaken to determine the influence of compost, bentonite and calcium oxide on the content of polycyclic aromatic hydrocarbons (PAHs) in soils polluted with petrol and diesel oil, using plants as phytoremediators. Contamination of soil with petrol and diesel oil caused an increase in the total PAHs in soil. The effect of diesel oil on the content of PAHs in soil was stronger than that of petrol in the treatments with spring barley and yellow lupine – maize, in reverse to spring rape – oat. Pollution of soil with petroleum substances led to the increased contribution of naphthalene to the total PAHs at the expense of other hydrocarbons. Bentonite and CaO produced an evidently stronger effect on soil properties than compost, in general causing a decline in the content of PAHs in soil. The phytoremediatory effect of plants was the most beneficial in the treatment with spring rape and oat, but the weakest in trials with yellow lupine and maize. Plants were particularly effective in soil polluted with petrol.

Keywords: oil-derived substances; neutralisation; PAHs; amendments; phytoremediation; soil contamination

Pollution of the environment with petroleum substances containing many highly toxic compounds is extremely dangerous to live organisms. Petroleum substances, for example, include aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs (Turrio-Baldassarri et al. 2004). Among the major sources of hydrocarbons spreading in the natural environment, beside combustion of solid and liquid fuels (Achten and Hofmann 2009), including the ones used for transportation (Liu et al. 2009), is accidental contamination during transport of petroleum products, such as diesel oil or petrol (Maliszewska-Kordybach et al. 2009). Due to their very slow migration and because of the persistence and insolubility of their molecules, PAHs accumulate and remain in soil for a very long time. It is worth noticing that PAHs are hardly biodegradable. They can undergo biotransformation by attaching to other organic compounds and entering biochemical cycles (Zabłocki et al. 1998). The uptake of PAHs by edible and fodder plants as well as their permeation to potable water may have serious ecological, sanitary and health-related consequences (U.S. EPA 2002, Wyszkowski and Wyszkowska 2005, Wyszkowska and Wyszkowski 2006, Vácha et al. 2010). It is therefore important to reduce the influence of PAHs on crops by introducing to soil various substances which increase degradation of hydrocarbons during the growing season of crops (Geissen et al. 2008, Wyszkowski and Sivitskaya 2013).

In view of the above, a series of experiments has been conducted in order to determine the influence of compost, bentonite and CaO on the content of PAHs in soils polluted with petrol and diesel oil, using plants as phytoremediators.

### MATERIAL AND METHODS

Methodology of the vegetative trials. A threeyear (2003–2005) plant growing experiment was carried out in a greenhouse at the University of Warmia and Mazury in Olsztyn (north-eastern Poland). The trials were performed in polyethylene pots, which were filled with 9.5 kg of soil each. Three types of typical Eutric Cambisols soil, originating from loamy sand and similar in physicochemical properties, were used for the pot trials. The variable factors comprised the type of a petroleum substance: non-lead petrol 95 (Pet) and diesel oil (DO), rates of petrol and diesel oil: 0 and 10 cm<sup>3</sup>/kg of soil, and type of a substance alleviating the negative influence of petrol or diesel oil on soil: compost (3%), bentonite (2%) and calcium oxide in the amount corresponding to 1 hydrolytic acidity (HAC<sub>1</sub>). In addition, the soil was enriched with aqueous solutions of macro- and micronutrients. Among the three soil amending substances, the compost had a particularly high content of PAHs, including FTH, BaA, CHR, BaP and BghiP. A detailed specification of soils, composition of the three soil amending substances and doses of macro- and micronutrients added to each pot can be found in other paper (Wyszkowska and Wyszkowski 2010). The following plants were tested with respect to the phytoremediation of soil polluted with petrol and diesel oil: spring barley (Hordeum vulgare L.) Polish cv. Ortega, which was grown until the full maturity phase, separating between grain, straw and roots - trial 1, spring rape (Brassica napus var. oleifera) Polish cv. Mazowiecki (main crop) and oat (Avena sativa L.) Polish cv. Borowik (aftercrop) – trial 2, and yellow lupine (Lupinus luteus L.) Polish cv. Parys (main crop) and maize (Zea mays L.) Polish cv. Scandia (aftercrop) - trial 3. Spring barley, oat, yellow lupine and maize were grown for green matter. Throughout the whole study, constant soil moisture at the level of 60% of water capillary capacity was maintained. The trials were designed with 4 replications. During the harvest of spring barley and the aftercrops (oat and maize), soil material was sampled for laboratory analyses.

Soil analysis and statistical computations. Soil samples were collected prior to the establishment of the experiment and after the harvest of the test plants (from each pot), then dried and passed through a sieve of the mesh size 1 mm. The prepared soil samples were analysed to determine the content of PAHs,

using high performance liquid chromatography (HPLC) with the GC/MS (SIM) method for analysis of the extracts; the soil samples were extracted according to ISO 13877 (1998E). According to the regulation of the Polish Ministry for the Environment (Regulation of Ministry of Environment, No. 165, 2002), content of 9 PAHs was determined: naphthalene - NAP; phenanthrene - PHE; anthracene - ANT; fluoranthene - FTH; benzo(a)anthracene - BaA; chrysene - CHR; benzo(a)fluoranthene -BaF; benzo(a)pyrene – BaP and benzo(ghi)perylene BghiP. Standard deviations were also calculated between the analyzed variables. The results of these determinations underwent statistical processing using a Statistica software package (Tulsa, USA) and applying a three-factor analysis of variance ANOVA.

### **RESULTS AND DISCUSSION**

The influence of petrol and diesel oil on the content of PAHs in soil. In the series without soil amending substances, an application of 10 cm<sup>3</sup> of petrol or diesel oil caused an increase in the concentration of sum of PAHs (Tables 1–3).

In the soil after spring barley harvest, in the objects polluted with petrol, the increase of sum of PAHs equalled 73%, whereas in those contaminated by diesel oil it raised by 172% relative to the control objects (not contaminated) (Table 1). In the same series, the highest increase among the nine analysed hydrocarbons was noted for two-ringed NAP in petrol-treated objects. In the soil after spring rape - oat harvest, in the series without soil amending substances, an application of 10 cm<sup>3</sup> of petrol or diesel oil per kg of soil caused an increase in the content of PAHs, with a much stronger increase in all the nine PAHs observed under the influence of petrol than diesel oil (Table 2). In the object treated with 10 cm<sup>3</sup> of petrol per kg of soil, the content of these PAHs rose by 31%. Stronger effect was noticed in the objects treated with diesel oil than with petrol in soil after the harvest of yellow lupine - maize (Table 3). The total of PAHs in this series of trials rose by 61% in the soil polluted with petrol and by as much as 306% in the soil with diesel oil. The exact value of the increase was highly varied between individual PAHs. The high increase in the total PAHs under the effect of diesel oil was attributable to the fact that the content of all PAHs rose in the variant including 10 cm<sup>3</sup> of diesel oil per kg of soil and

Table 1. Effect of petrol and diesel oil contamination on content of polycyclic aromatic hydrocarbons (PAHs) in soil after harvest of spring barley (*Hordeum vulgare* L.), in  $\mu g/kg$  dry mass

Dose of Pet or DO (cm <sup>3</sup> /kg of soil)		rol (Pet)	Diesel oil (DO)								
	substance neutralizing effect of Pet and DO										
	without substances	compost	bentonite	CaO	average	without substances	compost	bentonite	CaO	average	
2 and 3 rings PAHs											
Naphthalene – NAP											
0	1	1	1	31	9	1	1	1	31	9	
10	67	57	42	39	51	46	29	33	27	34	
Average	$34 \pm 3.7$	$29 \pm 2.9$	$22 \pm 2.7$	$35\pm3.3$	$30 \pm 3.3$	$24 \pm 2.7$	$15 \pm 2.4$	$17 \pm 1.4$	$29\pm1.6$	$21 \pm 2.0$	
Phenanthrene – PHE											
0	13	11	9	8	10	13	11	9	8	10	
10	9	9	8	9	9	23	14	28	34	25	
Average	$11\pm1.6$	$10\pm0.8$	$9 \pm 0.4$	$9 \pm 0.4$	$10\pm0.6$	$18 \pm 1.6$	$13\pm1.2$	$19 \pm 1.6$	$21 \pm 1.6$	$18 \pm 1.1$	
Anthracene – ANT											
0	1	2	2	2	2	1	2	2	2	2	
10	1	2	2	2	2	12	10	4	6	8	
Average	$1 \pm 0.06$	$2 \pm 0.1$	$2 \pm 0.09$	$2 \pm 0.6$	$2 \pm 0.08$	$7 \pm 0.5$	$6 \pm 0.3$	$3 \pm 0.2$	$4 \pm 0.2$	$5 \pm 0.3$	
4 rings PAHs											
Fluoranthene – FTH											
0	18	37	20	13	22	18	37	20	13	22	
10	8	12	6	16	11	20	18	19	15	18	
Average	$13 \pm 1.0$	$25\pm1.2$	$13 \pm 1.0$	$15\pm0.9$	$16 \pm 1.0$	$19 \pm 0.8$	$28\pm1.8$	$20 \pm 0.4$	$14 \pm 0.8$	$20 \pm 1.1$	
${\tt Benzo}(a) \\ {\tt anthracene}$	– BaA										
0	3	25	4	3	9	3	25	4	3	9	
10	5	9	5	5	6	16	10	8	3	9	
Average	$4 \pm 0.3$	$17\pm1.1$	$5 \pm 0.4$	$4 \pm 0.3$	$7 \pm 0.5$	$10 \pm 0.6$	$18 \pm 0.8$	$6 \pm 0.3$	$3 \pm 0.1$	$9 \pm 0.5$	
Chrysene – CHR											
0	9	36	9	8	16	9	36	9	8	16	
10	8	13	8	7	9	24	12	7	7	13	
Average	$9 \pm 0.4$	$25 \pm 2.3$	$9 \pm 0.4$	$8 \pm 0.4$	$12 \pm 0.9$	17 ± 1.0	$24 \pm 1.3$	$8 \pm 0.8$	$8 \pm 0.4$	$14 \pm 0.7$	
5 rings PAHs											
Benzo(a)fluoranthen	e – BaF										
0	1	6	2	1	3	1	6	2	1	3	
10	1	2	1	1	1	10	2	1	1	4	
Average	$1 \pm 0.03$	$4 \pm 0.2$	$2 \pm 0.3$	$1 \pm 0.08$	$2 \pm 0.1$	$6 \pm 0.2$	$4 \pm 0.2$	$2 \pm 0.4$	$1 \pm 0.07$	$3 \pm 0.2$	
Benzo(a)pyrene – Ba	ıP										
0	9	30	9	8	14	9	30	9	8	14	
10	5	11	6	5	7	17	23	32	9	20	
Average	$7 \pm 0.6$	$21 \pm 0.8$	$8 \pm 0.3$	$7 \pm 0.3$	$10 \pm 0.3$	$13 \pm 0.7$	$27 \pm 1.5$	21 ± 1.3	$9 \pm 0.4$	$17 \pm 1.0$	
6 rings PAH											
Benzo(ghi)perylene -	- BghiP										
0	9	29	8	5	13	9	29	8	5	13	
10	7	13	2	7	7	6	50	7	11	19	
Average	8 ± 0.8	$21 \pm 0.6$	$5 \pm 0.3$	$6 \pm 0.3$	$10 \pm 0.5$	$8 \pm 0.5$	$40 \pm 2.3$	$8 \pm 0.3$	8 ± 0.2	16 ± 0.8	
Sum of 9 PAHs											
0	64	177	64	79	96	64	177	64	79	96	
10	111	128	80	91	103	174	168	139	113	149	
Average	88 ± 5.9	$153 \pm 7.9$	$72 \pm 6.5$		99 ± 6.5	119 ± 8.9	$173 \pm 3.7$	$102 \pm 3.9$		$122 \pm 5.1$	
$LSD_{0.01}$		a – 1.5, b	– 1.5, c –	2.7, a ×	b - 2.1,	$a \times c - 3.8$ , b	$\times$ c $-$ 3.8,	$a \times b \times c$ –	- 5.3		

Values are average  $\pm$  standard deviation. LSD for: a – kind of petroleum substances; b – petroleum dose; c – kind of neutralizing substance

Table 2. Effect of petrol and diesel oil contamination on the content of polycyclic aromatic hydrocarbons (PAHs) in soil after harvest of spring rape (*Brassica napus* var. *oleifera*) – oats (*Avena sativa* L.) – aftercrop, in  $\mu$ g/kg dry mass

Dogo of Dat		trol (Pet)	Diesel oil (DO)							
Dose of Pet or DO		subst	effect of Pet and DO							
(cm <sup>3</sup> /kg of soil)	without substances	compost	bentonite	CaO	average	without substances	compost	bentonite	CaO	average
2 and 3 rings PAHs										
Naphthalene – NAP										
0	14	21	22	20	19	14	21	22	20	19
10	28	18	10	34	23	16	20	29	10	19
Average	$21 \pm 2.0$	$20 \pm 1.2$	$16 \pm 0.9$	$27 \pm 1.7$	$21 \pm 1.4$	$15 \pm 0.8$	$21 \pm 0.4$	$26 \pm 0.9$	$15 \pm 0.9$	$19 \pm 0.7$
Phenanthrene – PHE										
0	15	28	30	14	22	15	28	30	14	22
10	15	13	18	25	18	13	22	22	5	16
Average	$15 \pm 0.3$	$21 \pm 0.9$	$24 \pm 1.5$	$20 \pm 1.0$	$20 \pm 0.9$	$14 \pm 0.8$	$25 \pm 2.0$	$26 \pm 1.5$	$10 \pm 0.5$	$19 \pm 1.2$
Anthracene – ANT										
0	1	1	1	1	1	1	1	1	1	1
10	1	1	1	1	1	2	1	3	1	2
Average	$1 \pm 0.03$	$1 \pm 0.03$	$1 \pm 0.04$	$1 \pm 0.03$	$1 \pm 0.03$	$2 \pm 0.1$	$1 \pm 0.03$	$2 \pm 0.09$	$1 \pm 0.04$	$1 \pm 0.05$
4 rings PAHs										
Fluoranthene – FTH										
0	13	27	14	9	16	13	27	14	9	16
10	9	7	6	12	9	9	14	9	6	10
Average	$11 \pm 0.6$	$17 \pm 0.8$	$10 \pm 0.3$	$11 \pm 0.3$	$12 \pm 0.5$	$11 \pm 0.7$	$21 \pm 0.8$	$12 \pm 0.7$	$8 \pm 0.3$	$13 \pm 0.6$
Benzo(a)anthracene	– BaA									
0	1	1	1	1	1	1	1	1	1	1
10	1	1	1	1	1	1	3	1	1	2
Average	$1 \pm 0.03$	$1 \pm 0.03$	$1 \pm 0.04$	$1 \pm 0.03$	$1 \pm 0.03$	$1 \pm 0.02$	$2 \pm 0.3$	$1 \pm 0.01$	$1 \pm 0.2$	$1 \pm 0.02$
Chrysene – CHR										
0	1	2	1	2	2	1	2	1	2	2
10	4	5	1	1	3	4	6	1	1	3
Average	$3 \pm 0.1$	$4 \pm 0.1$	$1 \pm 0.06$	$2 \pm 0.1$	$2 \pm 0.1$	$3 \pm 0.1$	$4 \pm 0.2$	$1 \pm 0.03$	$2 \pm 0.05$	$2 \pm 0.07$
5 rings PAHs										
Benzo(a)fluoranthen	ie – BaF									
0	1	1	1	1	1	1	1	1	1	1
10	1	1	1	1	1	1	1	1	1	1
Average	$1 \pm 0.05$	$1 \pm 0.03$	$1 \pm 0.01$	$1 \pm 0.02$	$1 \pm 0.04$	$1 \pm 0.04$	$1 \pm 0.02$	$1 \pm 0.05$	$1 \pm 0.02$	$1 \pm 0.03$
Benzo(a)pyrene – Ba	ıΡ									
0	3	4	4	4	4	3	4	4	4	4
10	6	5	3	2	4	2	7	4	2	4
Average	$5 \pm 0.3$	$5 \pm 0.4$	$4 \pm 0.2$	$3 \pm 0.1$	$4 \pm 0.2$	$3 \pm 0.2$	$6 \pm 0.2$	$4 \pm 0.1$	$3 \pm 0.1$	$4 \pm 0.2$
6 rings PAH										
Benzo(ghi)perylene -	- BghiP									
0	3	6	2	6	4	3	6	2	6	4
10	3	6	4	5	5	4	10	6	1	5
Average	$3 \pm 0.2$	$6 \pm 0.2$	$3 \pm 0.1$	$6 \pm 0.2$	$4 \pm 0.2$	$4 \pm 0.1$	$8 \pm 0.3$	$4 \pm 0.2$	$4 \pm 0.2$	$5 \pm 0.2$
Sum of 9 PAHs							,			
0	52	91	76	58	69	52	91	76	58	69
10	68	57	45	82	63	52	84	76	28	60
Average	$60 \pm 3.8$	$74 \pm 5.8$	$61 \pm 2.7$	$70 \pm 3.7$	$66 \pm 3.8$	$52 \pm 1.9$	$88 \pm 2.9$	$76 \pm 1.1$		$65 \pm 2.2$
$LSD_{0.01}$		a – 0.9, b				× c – 2.2, b				

Values are average  $\pm$  standard deviation. LSD for: a – kind of petroleum substances; b – petroleum dose; c – kind of neutralizing substance

Table 3. Effect of petrol and diesel oil contamination on the content of polycyclic aromatic hydrocarbons (PAHs) in soil after harvest of yellow lupine ( $Lupinus\ luteus\ L.$ ) – maize ( $Zea\ mays\ L.$ ) – aftercrop, in  $\mu g/kg\ dry\ mass$ 

Dose of Pet		Pet	rol (Pet)			Diesel oil (DO)					
or DO	kind of substance neutralizing effect of Pet and DO										
(cm <sup>3</sup> /kg of soil)	without substances	compost	bentonite	CaO	average	without substances	compost	bentonite	CaO	average	
2 and 3 rings PAl											
Naphthalene – Na	AΡ										
0	1	1	1	1	1	1	1	1	1	1	
10	2	12	2	3	5	46	29	33	27	34	
Average	$2 \pm 0.1$	$7 \pm 0.2$	$2 \pm 0.1$	$2 \pm 0.1$	$3 \pm 0.1$	$24 \pm 1.1$	$15 \pm 1.0$	$17 \pm 0.9$	$14 \pm 0.7$	$17 \pm 0.9$	
Phenanthrene – P	HE										
0	17	34	23	25	25	17	34	23	25	25	
10	22	75	24	26	37	35	74	131	127	92	
Average	$20 \pm 0.9$	$55 \pm 1.8$	$24 \pm 0.4$	$26 \pm 0.4$	$31\pm1.1$	$26 \pm 1.3$	$54 \pm 1.9$	$77 \pm 4.0$	$76 \pm 3.9$	$58 \pm 2.5$	
Anthracene – AN	T										
0	1	1	1	1	1	1	1	1	1	1	
10	3	11	1	2	4	3	2	1	2	2	
Average	$2 \pm 0.1$	$6 \pm 0.3$	$1\pm0.05$	$2 \pm 0.09$	$3 \pm 0.1$	$2 \pm 0.1$	$2 \pm 0.08$	$1 \pm 0.06$	$2 \pm 0.1$	$2 \pm 0.09$	
4 rings PAHs											
Fluoranthene – F	ГН										
0	20	29	24	18	23	20	29	24	18	23	
10	39	262	52	18	93	81	127	242	266	179	
Average	$30 \pm 1.8$	$146 \pm 5.1$	$38 \pm 1.1$	$18 \pm 0.5$	$58 \pm 2.2$	$51 \pm 2.4$	$78 \pm 2.6$	$133 \pm 6.9$	$142 \pm 7.6$	$101 \pm 4.3$	
Benzo(a)anthrace	ne – BaA										
0	2	2	2	1	2	2	2	2	1	2	
10	2	96	1	1	25	12	7	16	13	12	
Average	$2 \pm 0.08$	$49 \pm 2.1$	$2 \pm 0.1$	$1 \pm 0.04$	$13 \pm 0.4$	$7 \pm 0.4$	$5 \pm 0.2$	$9 \pm 0.4$	$7 \pm 0.2$	$7 \pm 0.3$	
Chrysene – CHR											
0	1	6	4	4	4	1	6	4	4	4	
10	2	62	3	2	17	5	2	7	2	4	
Average	$2 \pm 0.09$	$34 \pm 1.1$	$4 \pm 0.2$	$3 \pm 0.1$	$11 \pm 0.4$	$3 \pm 0.1$	$4 \pm 0.1$	$6 \pm 0.2$	$3 \pm 0.1$	$4 \pm 0.1$	
5 rings PAHs											
Benzo(a)fluoranth	nene – BaF										
0	1	2	1	1	1	1	2	1	1	1	
10	1	16	1	1	5	2	4	9	7	6	
Average	$1 \pm 0.04$	$9 \pm 0.3$	$1 \pm 0.02$	$1 \pm 0.03$	$3 \pm 0.2$	$2 \pm 0.1$	$3 \pm 0.1$	$5 \pm 0.2$	$4 \pm 0.2$	$3 \pm 0.1$	
Benzo(a)pyrene –											
0	4	6	5	4	5	4	6	5	4	5	
10	2	66	2	2	18	5	9	12	6	8	
Average	$3 \pm 0.1$	$36 \pm 1.1$	$4 \pm 0.2$	$3 \pm 0.1$	$11 \pm 0.4$	$5 \pm 0.2$	$8 \pm 0.3$	$9 \pm 0.3$	$5 \pm 0.2$	$6 \pm 0.2$	
6 rings PAH											
Benzo(ghi)peryler	ne – BøhiP										
0	2	10	6	5	6	2	10	6	5	6	
10	6	46	4	4	15	10	17	9	16	13	
Average	$4 \pm 0.1$	$28 \pm 1.1$	$5 \pm 0.2$	$5 \pm 0.2$	$10 \pm 0.4$	$6 \pm 0.2$	14 ± 0.6	8 ± 0.3	11 ± 0.4	$9 \pm 0.4$	
Sum of 9 PAHs	1 - 0.1	20 ± 1.1	<i>5</i> ± 0.2	J ± 0.2	10 ± 0.1	0 ± 0.4	11100	0 - 0.0	11 ± 0.T	/ ± U₁T	
0	49	91	67	60	67	49	91	67	60	67	
10	79	646	90	59	219	199	271	460	466	349	
10	17										
Average	$64 \pm 2.2$	$369 \pm 18.8$	$79 \pm 6.4$	60 + 14	$143 \pm 7.5$	$124 \pm 3.8$	$181 \pm 6.4$	$264 \pm 7.1$	$263 \pm 9.8$	$208 \pm 7.8$	

Values are average  $\pm$  standard deviation. *LSD* for: a – kind of petroleum substances; b – petroleum dose; c – kind of neutralizing substance

their increments can be ordered as follows: BaP < BaF < PHE < ANT < FTH < CHR = BghiP < BaA < NAP. In the objects with petrol, in turn, the content of BaP decreased whereas that of BaA and BaF did not change under the influence of 10 cm<sup>3</sup>/kg. The content of the other PAHs increased in the following order: PHE < FTH < CHR = NAP < ANT = BghiP. Petrol and diesel oil caused changes in the mutual proportions of PAHs in their total concentration. High levels of PAHs in soil, especially 2- and 3-ringed ones, were noticed by Nganje et al. (2007). Baran and Oleszczuk (2001) reported that 2- to 4-ringed hydrocarbons, i.e. low molecular ones, mainly PHE and FTH, make up most (about 70%) of the global contamination with PAHs. A study completed by Kondras and Czępińska-Kamińska (2004) demonstrated that the content of PAHs in soil near gasoline stations could to some extent depend on physicochemical properties of soil, mainly the content of organic matter and pH of soil.

Effect of soil amending substances on the content of PAHs in soil. In the soil in which spring barley was grown, an application of any alleviating substance proved more efficient in objects polluted with diesel oil than in those with petrol (Table 1). Bentonite and CaO (in reverse to compost) in the pots contaminated with petrol or diesel oil depressed the content of PAHs in soil compared to the series without such soil amendments.

In the spring rape – oat cultivation, the content of sum of PAHs in soil significantly depended on the petrol and on the application of compost and bentonite, as well as it depended on the diesel oil and the addition of CaO (Table 2). In the objects polluted with 10 cm³ of petrol per kg of soil and amended with these substances, a lower total of PAHs was observed than in the non-amended variants. In the treatments with diesel oil and with an addition of compost or bentonite, reverse dependencies were observed.

Compost had the strongest impact on the total content of PAHs in the soil contaminated with petrol after the harvest of yellow lupine – maize (especially in the object with  $10 \text{ cm}^3/\text{kg}$ ), where it caused a very high increase in their content (Table 3). All substances (particularly bentonite and CaO) had the same effect on the total content of PAHs in soil. In the soil polluted with diesel oil, sum of PAHs increased after an application of bentonite or CaO, but an analogous increase was much smaller following an introduction of compost. Bentonite and

CaO had a similar effect on the content of PAHs in soil. Amendments had a strong effect on PAHs in objects without petrol and diesel oil, too.

The efficiency of the removal of petroleum pollutants found in the soil environment depends on many factors, including the extent to which PAHs are absorbed by the soil. The organic matter in soil plays a particularly positive role in this process (Thiele and Brümmer 1998). Increased sorption can very often stimulate strong binding of some of petroleum substances with the organic fraction and, to a lesser extent, with the mineral fraction of soil, consequently leading to the formation of residues of petroleum substances which are difficult to remove (Kästner et al. 1995). The structure of such bonds was not precisely examined although they reduce the mobility, biotoxicity and bioavailability of hydrocarbons in soil (Printz et al. 1995). By introducing some organic substance to soil (especially the easily decomposable one of the C:N ratio < 20) it is possible to produce a beneficial effect on the degradation of PAHs and reduction of their content in soil (Thiele and Brümmer 1998), which has been confirmed in the present research for some of the tested PAHs.

Luster-Teasley et al. (2009) found out that increased pH of soil has a positive effect on bioremediation of PAHs. In contrast, excessive soil moisture content produces an adverse influence of this process. In a study reported by Thiele and Brümmer (1998), the maximum degradation of PAHs was obtained by increasing the pH of an acidic soil to 6 after an application of lime fertilizers. It is difficult to find in the existing references many data concerning the influence of bentonite on the content of PAHs in petroleum polluted soil undergoing phytoremediation. Nonetheless, as bentonite has a positive influence on the growth, development and chemical composition of plants (Wyszkowski et al. 2004, Wyszkowski and Ziółkowska 2009) as well as on the microbiological properties of soil and activity of some soil enzymes (Wyszkowska and Wyszkowski 2010), we decided to test whether it would have any positive effect on the content of PAHs in soil contaminated with petrol and diesel oil. In the above presented study bentonite had a positive effect on soil pH. A positive effect of CaO, compost and bentonite on pH and other properties of soil were reported in paper published earlier (Wyszkowski and Ziółkowska 2011).

In some objects polluted with petrol and diesel oil added in dose of 10 cm<sup>3</sup>/kg of soil, but only

in the series with compost and much less often with bentonite and CaO, permissible values of PHE, FTH and BaP were exceeded. Such excessive levels were recorded for FTH and BaP in petrolcontaminated soil in the series with compost; for PHE in objects polluted with diesel oil in the series with bentonite and CaO and for FTH after an application of each amendment. However, in none of the experimental variants, the value of the total PAHs was higher than the permissible value established for the topmost layer of cultivated soils (Regulation of Ministry of Environment, No. 165, 2002). The content of individual PAHs in soil determined after the harvest of the test plants did not usually exceed 100 μg/kg (or 30 μg/kg for BaP), which is a similar result to that reported by Maliszewska-Kordybach et al. (2009), who found out that the concentrations of PAHs were lower than the binding limits in 90% of the analysed samples of Polish soils (Regulation of the Ministry of Environment, No. 165, 2002).

Contamination of soil with petrol and diesel oil caused an increase in the total PAHs in soil. The effect of diesel oil on the content of PAHs in soil was stronger than that of petrol in the treatments with spring barley and yellow lupine – maize. Reverse effects were noticed in soil after the harvest of oat. Pollution of soil with petroleum substances led to the increased contribution of naphthalene to the total PAHs at the expense of other hydrocarbons. Bentonite and calcium oxide produced an evidently stronger effect on soil properties than compost, in general causing a decline in the content of PAHs in soil. The phytoremediatory effect of plants was the most beneficial in the treatment with spring rape and oat, but the weakest – in trials with yellow lupine and maize. Plants were particularly effective in soil polluted with petrol. The value of the total PAHs in soil after crop harvest was lower than the permissible values set for soils in Poland. It was only in the treatment with yellow lupine and maize that in some objects polluted with petrol and diesel oil the levels of phenanthrene, fluoranthene and benzo(a)pyrene exceeded the permissible amounts.

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