Supporting information:

Combined effects of plant cultivation and sorbing carbon amendments on freely dissolved PAHs in contaminated soil

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Analysis of physico-chemical properties of soil, biochars and activated carbon

The pH was measured potentiometrically in 1 M KCl after 24 h in the liquid/soil ratio of 10 (w/v). The cation exchange capacity (CEC, expressed as sum of the bases Ca, Mg, K, Na) was determined in the 0.1 M HCl extraction. The amounts of carbon, hydrogen and nitrogen were determined using a CHN equipment (Perkin–Elmer 2400, USA). The total organic carbon content (TOC) was determined by the dry combustion method using a TOC-VCSH (SHIMADZU, Japan) with a Solid Sample Module SSM-5000. The DOC content was determined according to Jones and Willett.¹ Black carbon in soils was quantified using the chemo-thermal oxidation (CTO) method adapted for soil by Agarwal and Bucheli.² The textural characteristics of the biochars were recorded with a Micromeritics ASAP 2405 N₂ adsorption analyser (USA) by performing low-temperature (77.4 K) nitrogen adsorption–desorption isotherms. The specific surface area (S_{BET}) of the AC and the biochars was determined according to the Brunauer – Emmett – Teller isotherm.

Adsorption experiment

The adsorption experiment was carried out by the method proposed by Hale et al.³ AC or biochar sample (50 mg) were added to 50 mL glass flasks with glass lids. The glass vials were tightly sealed and did not leak during the experiment. Millipore water (40 mL) with sodium azide (20 mg L⁻¹) to eliminate any possible effect of remaining microorganisms and strips of 55-µm thick polyoxymethylene (POM) passive samplers (0.3 g for all batches) were added to vials. Prior to use, POM samplers were cleaned by cold extraction overnight in methanol, then in heptane, rinsing thoroughly with Millipore water and finally drying. Batches were spiked with phenanthrene (PHE), pyrene (PYR) or benzo[a]pyrene (BaP) in methanol. The amount of spiked cosolvent (100 μ l) did not exceed 0.25 % of the water volume and therefore the cosolvent effect was minimal in this system. To determine the initial concentration of PHE/PYR/BaP present in AC/biochar to glass flasks only AC/biochar + POM + water were added. Flasks were rolled end over end for 21 days at 1 RCF, after which POM samplers were removed, cleaned with Millipore water and wiped with a tissue to ensure they were dry and visibly clean. POM samplers were extracted in 20 mL of 20:80 acetone:heptane for 2 days. The solvent was reduced to about 1 mL using rotary vacuum concentrator RVC 2-25 CD plus (Martin Christ, Germany). A quantitative analysis of PAHs was carried out on Thermo Scientific Trace 1 300 Gas Chromatograph equipped with a Restek Rxi-5ms Column (length 30 m, 0.25 mm id and 0.25 µm film thickness). Detailed information about PAHs analysis is presented below.

The concentration of PHE/PYR/BaP on POM passive samplers was calculated according to the equation (1):

$$C_{POM} = \frac{C_{extract} \cdot V_{extract}}{m_{POM}} \quad (1)$$

where $C_{extract}$ (ng L⁻¹) is the concentration of PAH determined via GC-MS, $V_{extract}$ is the volume of solvent (L) and m_{POM} (kg) is the mass of POM passive samplers.

The concentration of PHE, PYR or BaP in water after 21 days of mixing was calculated on the basis of equation (2):

$$C_w = \frac{C_{POM}}{K_{POM}} \qquad (2)$$

where C_w (ng L⁻¹) is the aqueous phase concentration of PHE, PYR or BaP, K_{POM} (L kg⁻¹) is the predetermined POM-water partitioning coefficient specific to PHE, PYR or BaP obtained from Hawthorne et al.⁴ and C_{POM} (ng kg⁻¹) is the measured PAH concentration in POM strips.

The concentration of PHE, PYR or BaP on AC/biochar was calculated on the basis of equation:

$$C_s = \frac{C_{int} - C_w}{m_{sorbent}} V_r \tag{3}$$

where C_s (µg kg⁻¹) is PHE, PYR or BaP on AC/biochar, C_{int} (µg L⁻¹) is the initial concentration of PHE, PYR or BaP in the water solution, C_w (ng L⁻¹) is the aqueous phase concentration of PHE, PYR or BaP, V_r (L) is the volume of solution, $m_{sorbent}$ (kg) is the mass of sorbent used for the experiment.

The sorption data were fitted with Freundlich sorption isotherm equation (logarithmic form):

$$log q_e = log K_F + n log C_e$$
 (4)

where q_e is the solid-phase concentration ($\mu g/kg$), C_e is the solution phase concentration ($\mu g/L$), K_F is the sorption affinity parameter (($\mu g/kg$)/($\mu g/L$)n), *n* is the nonlinear coefficient, The fitting was processed with Sigmaplot 10.0.

Determination of total PAHs content

The samples were extracted with hexane in Soxhlet for 36 h, 1 mL of isooctane was added as a keeper to concentrate the extracts to 1 mL using a rotary vacuum concentrator RVC 2–25 CD plus (Martin Christ, Germany). Then, the soil, biochar, activated carbon were subjected to the clean-up procedure (liquid-liquid partitioning) according to Brändli et al. (2006).⁵ After liquid-liquid partitioning, the recollected phase was reduced and applied to an open micro glass column (150 mm × 7 mm i.d.) filled with (from bottom to top) glass wool, deactivated silica gel (10% milli-Q water, 3 cm), water free sodium sulphate, and prewashed with 5 mL heptane. The extract was eluted with 10 mL of heptane. After the clean-up the extracts were concentrated to 0.5 mL, transferred into the vials and each sample was spiked with 20 μ L of a TTB (1,3,5-tri-tert-butylbenzene) solution of 6.1 μ g/mL.

The final concentrated extracts analyzed using gas chromatograph (Trace 1300) mass spectrometry (ISQ LT) (GC - MS, Thermo Scientific). The GC - MS was equipped with a single quadrupole and used under the selected ion monitoring mode. A Rxi[®]-5ms crossbond[®] 5% diphenyl and 95% dimethyl polysiloxane fused capillary column (30 m x 0.25 mm ID x 0.25 µm film thickness) from Restek (USA) was used with helium as the carrier gas at a constant flow rate of 1.5 ml/min. The GC oven temperature was programmed to ramp from 75°C (hold time – 0.5 min) to 245°C at 25°C/min, then to 300°C at 4°C/min (hold time – 1.0 min). The injector temperatures were 310°C. The detection was performed with a Thermo Scientific ISQ LT mass spectrometer in the electron impact mode with a -70 eV ionization energy and a dwelling time of 22 ms. Sixteen PAHs from US EPA list were determined: NAP - naphthalene; ACE - acenaphthylene; AC - acenaphthene; FL - fluorene; PHEN -ANT - anthracene; FLUO - fluoranthene; PYR - pyrene; BaA phenanthrene; benzo[*a*]anthracene; BbF – benzo[*b*]fluoranthene; CHR chrysene; BkF _ benzo[k]fluoranthene; BaP- benzo[a]pyrene; IcdP- indeno[1,2,3-cd]pyrene; DahA – dibenz[*a*,*h*]anthracene; BghiP – benzo[*ghi*]perylene.

The linearity ($R^2 > 0.99$) was given for a calibration from 10 to 2500 ng/mL and for each PAH compound. The limits of quantification (LOQ) ranged from 0.0002 (IcdP) to 0.3110 (NAP) ng/L for POM and 0.1 (CHR)–0.7 (DahA) µg/kg dry weight (dw) for total PAH concentrations and was obtained from three times the limit of detection (LOD). Blanks were run for total PAH concentrations (thimble filled with Na₂SO₄) and for the Cfree (POM strips but no sample). The recoveries were quantified by the deuterated internal standards (added before extraction) to the recovery standard (TTB) over the same ratio in the calibration. The recoveries ranged from 77 to 108 % for individual PAHs. The reported results have not been corrected for losses.

Quality assurance and quality control (QA/QC)

All samples were taken according to the PN-ISO 10381-2:2007P (ISO 10381-2:2002 - Soil quality -- Sampling -- Part 2: Guidance on sampling techniques, 2002). Chemical analyses were conducted at the University of Maria Skłodowska-Curie of Lublin (UMCS, Poland) in Department of Environmental Chemistry and Analytical Laboratory UMCS. The Analytical Laboratory UMCS is accredited by the Polish Centre for Accreditation (PCA). The procedures and methods of the chemical tests in lab were controlled according to existing standards or published papers. The QA/QC checks of the testing instruments (GC-MS, pH meter, TOC-VCSH etc.) in lab were conducted during and after installation by the supplier. To ensure quality assurance and quality control (QA/QC), we analyzed a blank sample, duplicate sample (n=3) and a standard reference material (PAHs - Loamy Sand, Sigma Aldrich) with each batch of samples. The all analytical instruments were also calibrated in the lab before the chemical analysis. Blank sample values were very low or below detection limits for the corresponding method. For each PAHs, the response factor percent relative standard deviations (% RSDs) typically were 4 to 15% and always less than 24%.

Compound	$log~\mathrm{K_F}$	п	Na	\mathbb{R}^2
	(mg kg ⁻¹)(mg L ⁻¹) ⁻ⁿ			
Biochar:				
Phenanthrene	5.13	0.684	8	0.950
Pyrene	5.53	0.630	8	0.949
Benzo[a]pyrene	6.34	0.631	8	0.948
AC:				
Phenanthrene	5.68	0.845	8	0.996
Pyrene	5.94	0.774	8	0.998
Benzo[<i>a</i>]pyrene	7.00	0.718	8	0.991

Table S1. Freundlich isotherm parameters for phenanthrene, pyrene and benzo[*a*]pyrene sorption by biochar and activated carbon

^a Number of data points.

PAHs			No plants					Willow		
	0	3	6	12	18	0	3	6	12	18
NA	217±20	216±24	220±33	216±31	217±22	229±27	220±21	220±32	219±36	221±24
ACE	10.2±1.0	9.3±1.1	9.8±1.0	9.9±1.2	9.3±1.3	9.3±1.2	9.5±0.8	9.3±1.5	9.1±1.3	10.2±1.2
AC	23.5±3.1	22.1±3.1	21.6±3.0	22.8±3.4	23.4±3.4	24.2±2.4	24.1±2.8	24.6±2.2	24.7±2.0	21.9±3.1
FL	13.9±1.4	14.0±2.1	13.4±1.5	13.0±1.9	12.9±1.9	12.9±1.8	12.5±1.8	13.7±1.4	12.2±1.3	12.3±2.0
PHEN	26.9±3.64	28.5±3.3	30.9±4.0	28.7±3.2	29.0±2.6	35.6±5.2	33.5±3.5	33.2±5.6	34.0±3.2	34.9±4.4
ANT	11.1±1.3	9.0±1.1	9.2±1.3	11.0±1.3	11.2±1.5	10.1±1.4	9.2±1.5	8.1±1.0	6.5±0.8	9.5±1.2
FLUO	27.8±3.0	25.7±2.8	21.1±3.0	19.2±2.0	17.5±2.2	26.6±3.2	24.3±2.9	24.6±4.0	25.3±2.6	24.2±2.7
PYR	18.6±1.8	20.4±2.3	18.6±2.6	19.8±3.1	18.9±1.6	19.8±2.0	19.2±2.1	19.1±2.6	20.2±2.6	16.6±2.5
BaA	1.54±0.19	0.71±0.12	0.85±0.06	0.68 ± 0.09	1.42±0.17	2.01±0.29	1.05±0.11	1.24±0.15	1.06 ± 0.08	1.00±0.16
CHR	2.89±0.35	1.90±0.27	1.96±0.18	1.53±0.11	2.02±0.31	4.07±0.65	2.69±0.37	3.09±0.30	2.65±0.40	2.10±0.19
BbF	0.80±0.12	0.43±0.06	0.23±0.03	0.23±0.02	0.26±0.03	1.10±0.16	0.81±0.12	0.72 ± 0.06	0.66 ± 0.07	0.63±0.09
BkF	0.41 ± 0.06	0.21±0.04	0.12 ± 0.02	0.09 ± 0.01	0.09 ± 0.01	0.62 ± 0.08	$0.44{\pm}0.06$	0.41 ± 0.05	$0.39{\pm}0.06$	0.37 ± 0.05
BaP	0.58 ± 0.08	0.34 ± 0.05	0.19±0.03	0.27 ± 0.04	0.27 ± 0.04	0.35 ± 0.04	$0.30{\pm}0.04$	0.26 ± 0.04	0.25 ± 0.04	$0.24{\pm}0.03$
IcdPd	0.07 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.08 ± 0.01	0.11 ± 0.01	0.09 ± 0.01	$0.10{\pm}0.01$	0.09 ± 0.01	0.08 ± 0.01
DahA	0.01 ± 0.001	0.02 ± 0.001	0.01 ± 0.001	0.02 ± 0.001	0.01 ± 0.001	0.03±0.001	0.02 ± 0.001	$0.02{\pm}0.001$	0.02 ± 0.001	0.01 ± 0.001
BghiP	0.06 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.03 ± 0.001	0.02 ± 0.001	0.05±0.01	0.06±0.01	0.06±0.01	0.04 ± 0.001	0.04±0.01

Table S2. The individual Cfree PAHs content in no planted and under willow cultivation control soil

PAHs			Grass					Clover		
	0	3	6	12	18	0	3	6	12	18
NA	219±34	212±35	221±24	221±34	221±30	225±34	225±29	227±36	226±36	228±27
ACE	9.02±1.30	8.56±1.05	9.96±1.30	5.87±0.51	7.09 ± 0.92	6.61±0.68	8.69±1.21	8.26±1.23	8.49±1.18	7.10±0.53
AC	21.7±2.9	21.2±3.5	21.5±2.9	25.2±3.1	23.6±1.8	24.7±2.0	25.1±2.4	20.5±3.5	21.1±2.9	24.1±3.6
FL	11.1 ± 0.8	13.4±1.5	12.5±1.2	13.4±2.0	14.9±1.9	20.1±2.3	16.7±2.4	14.2±1.6	16.8±2.7	16.8±2.0
PHEN	39.9±4.4	41.8±5.0	41.2±6.3	40.7±4.6	40.3±3.8	33.7±4.5	33.3±5.4	35.6±5.1	32.9±5.7	33.4±5.4
ANT	9.05±1.31	5.98±0.74	10.4±1.2	3.49±0.41	8.36±1.17	6.59±0.89	8.38±1.29	6.86±0.94	7.80 ± 0.88	7.91±1.0
FLUO	25.2±3.7	23.9±3.6	22.7±2.4	23.2±2.6	19.0±2.2	19.6±1.6	18.2±2.7	25.0±2.4	23.0±2.3	20.3±1.9
PYR	17.0±2.5	18.1±2.9	17.2±2.4	15.6±1.8	18.4±2.6	19.5±1.2	17.2±2.3	18.7±2.9	16.1±1.6	17.0±2.1
BaA	1.28 ± 0.11	1.04±0.16	1.33±0.15	0.81±0.12	0.72 ± 0.11	1.75±0.22	1.08±0.10	1.08±0.16	0.81±0.10	0.86±0.11
CHR	2.66±0.35	2.79±0.28	3.04±0.32	1.88±0.26	1.75±0.21	3.42±0.45	2.68±0.43	2.60±0.38	2.01±0.31	2.07±0.27
BbF	0.51±0.08	0.49 ± 0.06	0.45 ± 0.06	0.47 ± 0.08	0.42 ± 0.05	1.00 ± 0.12	0.85±0.13	0.83±0.09	0.72±0.11	0.65±0.10
BkF	0.27 ± 0.03	0.21 ± 0.01	0.18 ± 0.01	0.15 ± 0.02	0.15 ± 0.02	0.40 ± 0.07	0.31±0.03	0.25±0.03	0.21 ± 0.02	0.11 ± 0.02
BaP	0.27 ± 0.03	0.23 ± 0.04	0.22 ± 0.03	$0.20{\pm}0.02$	$0.24{\pm}0.02$	0.68±0.10	0.44 ± 0.07	0.42 ± 0.06	0.39±0.06	0.38±0.06
IcdPd	0.08 ± 0.01	0.08 ± 0.01	0.09 ± 0.01	0.07 ± 0.01	0.06 ± 0.01	0.07 ± 0.01	0.07 ± 0.01	0.07 ± 0.01	0.07 ± 0.01	0.06 ± 0.001
DahA	$0.02{\pm}0.001$	0.02 ± 0.001	0.03 ± 0.001	0.02 ± 0.001	$0.02{\pm}0.001$	0.01 ± 0.001				
BghiP	0.03 ± 0.001	0.02 ± 0.001	0.03±0.001	0.03±0.001	0.03 ± 0.001	0.05±0.01	0.04±0.001	0.04±0.001	0.04±0.01	0.05±0.01

Table S3. The individual Cfree PAHs content in under grass and clover cultivation control soil

PAHs			No plants					Willow		
	0	3	6	12	18	0	3	6	12	18
NA	220±18	187±28	170±6	125±15	82.3±6.6	217±29	213±27	169±19	107±15	76.2±7.5
ACE	11.2±1.3	8.87±1.44	4.42±0.62	6.02 ± 0.85	5.51±0.79	10.3±0.9	6.93±1.00	6.58±0.77	3.47±0.35	1.44±0.36
AC	19.0±2.9	18.5±2.5	9.29±1.12	9.03±0.98	5.27±0.71	14.2±1.9	12.4±1.5	10.5±1.3	9.03±1.32	5.70±2.20
FL	10.2±1.6	14.2±2.0	5.79±0.94	5.33±0.68	3.57±0.29	11.9±1.7	8.95±0.76	7.87±1.12	6.73±1.05	5.69±0.86
PHEN	29.6±3.7	22.0±3.5	14.5±2.0	6.77±0.99	6.67±0.69	26.7±1.8	24.9±3.9	22.8±2.9	22.0±1.8	12.0±4.3
ANT	6.48±1.05	6.99±0.91	5.77±0.78	3.12±0.23	2.91±0.41	6.33±0.99	5.84±0.68	5.77±1.00	3.30±0.48	2.75±0.77
FLUO	21.0±2.3	18.9±2.5	17.2±2.7	17.6±2.2	17.0±2.2	22.0±2.8	18.6±2.5	20.4±2.9	19.5±1.4	19.6±2.0
PYR	15.1±2.0	14.9±1.6	13.0±1.2	12.6±1.8	12.6±1.2	18.0±2.8	17.5±2.3	15.2±1.8	14.6±1.4	11.9±1.3
BaA	1.07±0.14	1.03±0.15	0.42 ± 0.06	0.81±0.12	0.74±0.12	0.94±0.12	0.88 ± 0.07	0.91±0.12	0.62 ± 0.08	0.50±0.04
CHR	2.25±0.21	2.69±0.26	1.32±0.20	2.32±0.32	1.89±0.27	1.96±0.29	1.65±0.24	1.27±0.21	1.67±0.22	1.29±0.13
BbF	0.65 ± 0.08	0.38±0.06	0.23±0.03	0.214±0.02	0.25±0.12	0.60±0.10	0.34±0.03	0.28±0.04	0.21±0.03	0.29±0.04
BkF	0.42 ± 0.04	0.09 ± 0.01	$0.034{\pm}0.02$	0.031 ± 0.001	0.03 ± 0.02	0.31±0.05	0.21±0.03	0.07 ± 0.01	0.06 ± 0.01	0.07 ± 0.01
BaP	0.38 ± 0.06	0.32 ± 0.04	$0.24{\pm}0.03$	0.188±0.03	0.14 ± 0.01	0.23±0.03	0.11 ± 0.01	0.12 ± 0.02	$0.10{\pm}0.02$	0.08 ± 0.01
IcdPd	0.07 ± 0.01	0.08 ± 0.01	0.042 ± 0.01	0.047 ± 0.01	0.054 ± 0.001	0.05±0.01	$0.04{\pm}0.01$	0.05 ± 0.001	0.03 ± 0.01	$0.02{\pm}0.001$
DahA	0.01 ± 0.001	0.02 ± 0.001	0.01 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	0.01±0.001	0.01 ± 0.001
BghiP	0.04 ± 0.01	0.02 ± 0.001	0.03 ± 0.001	0.03 ± 0.001	0.037 ± 0.01	0.04 ± 0.001	0.04 ± 0.001	$0.04{\pm}0.001$	0.03±0.001	0.04 ± 0.01

Table S4. The individual Cfree PAHs content in no plants and willow cultivation biochar-amended soil

PAHs			Grass					Clover		
	0	3	6	12	18	0	3	6	12	18
NA	195±28	166±16	163±25	173±27	81.4±7.7	226±25	193±15	176±21	129±19	86.3±11.0
ACE	10.2±1.4	9.07±1.07	6.23±0.79	3.36±0.33	2.78±0.46	9.41±1.51	9.49±1.48	7.69±1.21	6.14±0.55	4.28±0.57
AC	24.2±2.2	17.6±1.9	15.3±2.4	9.33±1.43	7.01±0.61	19.5±2.3	18.7±1.6	16.5±2.3	13.5±1.4	9.19±1.34
FL	10.7±1.7	7.18±0.84	6.92±0.62	2.96±0.31	2.00±0.25	18.1±2.0	8.23±1.17	5.04±0.77	2.63±0.41	2.24±0.28
PHEN	25.6±3.9	15.6±2.3	14.0±1.5	10.8±1.1	11.1±2.8	28.1±3.1	19.6±2.4	16.4±2.9	9.57±1.48	4.04±0.45
ANT	6.37±0.85	6.30±0.61	3.64±0.34	1.57±0.15	2.81±0.41	5.22±0.81	2.48±0.28	1.45±0.22	0.38±0.04	0.21±0.03
FLUO	20.2±2.3	18.5±2.9	15.0±2.1	9.86±1.30	8.93±1.33	19.3±3.3	16.0±2.0	12.0±1.8	11.4±1.4	7.33±0.76
PYR	15.3±2.1	13.7±1.5	11.7±1.1	7.57±1.18	6.73±1.04	13.9±2.1	12.7±1.6	5.57±0.61	5.55±0.72	5.92±0.78
BaA	1.00±0.16	0.59 ± 0.09	0.56 ± 0.08	0.24 ± 0.04	$0.19{\pm}0.02$	1.03±0.09	0.78±0.10	0.84±0.13	0.61±0.08	0.31±0.04
CHR	2.05±0.16	1.69±0.24	1.44±0.14	0.78±0.11	0.67 ± 0.07	2.17±0.26	1.90±0.23	0.94±0.13	0.90±0.14	0.82±0.10
BbF	0.45±0.07	0.29±0.04	0.20±0.03	0.17±0.01	0.10±0.01	0.51±0.07	0.33±0.05	0.24±0.02	0.21±0.01	0.19±0.02
BkF	0.21±0.03	0.17±0.02	0.09±0.01	0.04 ± 0.001	0.02 ± 0.001	0.35±0.04	0.12±0.001	0.04 ± 0.001	0.04 ± 0.001	0.03±0.001
BaP	0.23±0.02	0.17±0.02	0.07 ± 0.01	0.04 ± 0.01	0.03 ± 0.001	0.29±0.03	0.14 ± 0.02	0.03±0.001	0.02 ± 0.001	0.03±0.001
IcdPd	0.06 ± 0.001	0.06 ± 0.01	0.05±0.01	0.04 ± 0.001	0.02 ± 0.001	0.06±0.01	0.05 ± 0.001	0.03 ± 0.001	0.03 ± 0.001	0.02 ± 0.001
DahA	0.02 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	0.00	0.02 ± 0.001	0.00	0.01 ± 0.001	0.01 ± 0.001
BghiP	0.03±0.01	0.03 ± 0.001	0.02 ± 0.001	0.03±0.001	0.02 ± 0.001	0.04±0.01	0.03±0.001	0.03±0.001	0.02 ± 0.001	0.01±0.001

Table S5. The individual Cfree PAHs content in under grass and clover cultivation biochar-amended soil

PAHs			No plants					Willow		
	0	3	6	12	18	0	3	6	12	18
NA	219±16	191±10	144±12	113±8	54±5	186±26	178±20	137±13	53.6±6.6	37.3±4.4
ACE	9.69±1.45	9.59±0.96	9.54±1.19	3.42±0.33	3.36±0.52	9.33±1.41	5.59±0.53	3.41±0.53	0.74±0.10	0.37±0.07
AC	20.9±3.0	19.3±2.5	19.3±2.3	8.48±0.96	7.76±0.89	9.16±1.42	5.05±0.74	3.37±0.49	1.81±0.15	0.58 ± 0.08
FL	10.2±1.0	11.2±1.5	11.2±1.7	4.29±0.37	1.33±0.21	9.02±0.98	7.28±0.71	4.89±0.65	0.93±0.07	0.55±0.08
PHEN	25.6±3.0	25.8±2.6	25.7±4.0	1.19±0.15	1.18±0.12	17.7±2.5	11.7±1.5	6.35±0.65	1.93±0.27	0.59 ± 0.05
ANT	0.63±0.10	0.56±0.05	0.48 ± 0.06	0.22±0.03	0.44 ± 0.06	4.54±0.69	3.83±0.47	3.49±0.45	1.37±0.17	0.39±0.05
FLUO	$0.44{\pm}0.05$	0.25±0.04	0.18±0.03	$0.14{\pm}0.02$	0.10 ± 0.01	2.41±0.32	1.26±0.18	0.16±0.02	0.11±0.01	0.09±0.01
PYR	3.28±0.35	3.93±0.58	3.44±0.42	0.38±0.06	0.31±0.04	1.25±0.12	0.73±0.08	0.42 ± 0.04	0.30±0.04	0.19±0.03
BaA	0.01 ± 0.001	0.00	0.00	0.00	0.01 ± 0.001	0.01 ± 0.001	0.00	0.00	0.00	0.00
CHR	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	0.13±0.01	$0.02{\pm}0.001$	0.00	0.00	0.00
BbF	0.01±0.001	0.01 ± 0.001	0.00	0.00	0.00	0.02 ± 0.001	0.00	0.00	0.00	0.00
BkF	0.00	0.00	0.00	0.00	0.00	0.09 ± 0.01	0.00	0.00	0.00	0.00
BaP	0.10 ± 0.01	0.06 ± 0.01	0.05 ± 0.01	0.048 ± 0.01	0.01 ± 0.001	0.16±0.03	0.03 ± 0.001	0.03 ± 0.001	0.12±0.02	0.00
IcdPd	0.001 ± 0.0001	0.002 ± 0.001	0.002 ± 0.001	0.001 ± 0.001	0.001 ± 0.0001	0.022 ± 0.001	0.006 ± 0.001	0.005 ± 0.001	$0.004{\pm}0.001$	0.002 ± 0.001
DahA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BghiP	0.004 ± 0.001	0.003±0.001	0.00	0.00	0.00	0.008 ± 0.001	0.00	0.00	0.00	0.00

Table S6. The individual Cfree PAHs content in no plants and willow cultivation AC-amended soil

PAHs			Grass					Clover		
	0	3	6	12	18	0	3	6	12	18
NA	201±25	170±21	168±26	159±21	52.0±8.5	205±29	125±20	93.6±10.4	61.2±9.2	51.1±5.3
ACE	9.55±1.24	9.52±1.47	6.50±1.10	0.87 ± 0.09	0.25±0.03	8.02±1.01	5.51±0.86	3.01±0.39	2.31±0.33	1.75±0.18
AC	20.3±2.8	16.8±2.5	10.7±1.1	1.87±0.25	1.36±0.11	16.4±2.7	16.0±2.1	11.6±1.0	7.87±0.76	4.24±0.65
FL	10.4±1.5	9.11±0.79	7.95±1.06	0.93±0.10	0.99 ± 0.07	7.69±1.12	6.80±0.73	6.40±0.77	4.78±0.49	2.35±0.24
PHEN	23.5±2.8	18.8±1.5	13.5±1.8	1.07±0.15	0.84±0.13	26.0±3.0	20.7±2.6	7.59±0.97	6.15±0.42	3.28±0.23
ANT	0.62 ± 0.10	0.73±0.11	0.45 ± 0.05	0.00	0.50±0.07	6.89±0.60	3.78±0.58	1.38±0.11	2.28±0.29	2.36±0.31
FLUO	9.25±1.60	9.07±1.40	3.16±0.52	0.22 ± 0.03	$0.09{\pm}0.01$	5.19±0.41	1.19±0.15	0.19±0.03	0.13±0.02	$0.10{\pm}0.01$
PYR	6.32±0.91	2.62±0.23	0.41 ± 0.04	0.32 ± 0.03	0.25±0.03	2.25±0.18	0.92±0.12	0.21±0.03	0.22±0.03	0.21±0.03
BaA	0.01 ± 0.001	0.00	0.00	0.00	0.00	0.30 ± 0.05	0.09±0.01	0.01 ± 0.001	0.00	0.00
CHR	0.01 ± 0.001	0.01 ± 0.001	0.00	0.00	0.00	0.90 ± 0.07	0.10±0.01	0.01 ± 0.001	0.00	0.00
BbF	0.43 ± 0.06	0.29±0.04	0.14 ± 0.02	0.00	0.00	0.01 ± 0.001	0.00	0.00	0.00	0.00
BkF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaP	0.12 ± 0.01	0.06 ± 0.01	0.03 ± 0.001	0.03 ± 0.001	0.00	0.08 ± 0.01	0.13 ± 0.02	$0.04{\pm}0.001$	0.04 ± 0.02	0.013 ± 0.001
IcdPd	0.00	0.00	0.00	0.00	0.00	0.010 ± 0.001	0.009 ± 0.001	0.007 ± 0.001	0.006±0.001	0.002 ± 0.0001
DahA	0.00	0.00	0.00	0.01 ± 0.001	0.00	0.00	0.00	0.003±0.001	0.024±0.001	0.003±0.001
BghiP	0.00	0.00	0.00	0.00	0.00	0.009±0.001	0.00	0.00	0.00	0.00

Table S7. The individual Cfree PAHs content in under grass and clover cultivation AC-amended soil

	No plants	Grass	Clover	Willow
No amendment	×	×	×	×
Biochar	×	×	×	×
Activated carbon	×	×	×	×

Figure S1. The general scheme of the field experiment



Figure S2. Adsorption isotherms of phenanthrene (Phen), pyrene (Pyr) and benzo[*a*]pyrene (BaP) on native biochar (BC) and activated carbon (AC) used in the experiment



Figure S3. Log K_{TOC} values (L/Kg) for PAHs measured in present experiment comparing to recommended K_{TOC} values used by the US EPA for sediments [4], RIVM for soils and sediment [5] and Raoult's Law Coal Tar sorption model [6].



Figure S4. The reduction (%) of C_{free} PAHs after biochar or AC-soil amendment comparing to the control soil at the beginning of the experiment (top panel) and after 18-months (lower panel). * - means statistically significant differences compared to control soil (non-amended soil).



Figure S5. The content of $\Sigma 16 C_{\text{free}}$ PAHs in control (left panel), BCW- (middle panel) and AC-amended soil (right panel) depending on the plants cultivated. Error bars represent standard deviation error (SD, *n*=3 extractions).



Figure S6. The content of individual groups of C_{free} PAHs in control (left panel), BCW-(middle panel) and AC-amended soil (right panel) depending on the plants cultivated. Error bars represent standard deviation error (SD, n=3 extractions).



Figure S7. Changes of individual groups of C_{free} PAHs in experiment with grass in control (non- amended) or activated carbon (AC)/biochar (BCW)-amended soil. Error bars represent standard deviation error (SD, n=3 extractions).



Figure S8. Changes of individual groups of C_{free} PAHs in experiment with clover in control (non-amended) or activated carbon (AC)/biochar (BCW)-amended soil. Error bars represent standard deviation error (SD, n=3 extractions).



Figure S9. Changes of individual groups of C_{free} PAHs in experiment with willow in control (non-amended) or activated carbon (AC)/biochar (BCW)-amended soil. Error bars represent standard deviation error (SD, *n*=3 extractions).

REFERENCES

- Jones, D.; Willett, V. Experimental Evaluation of Methods to Quantify Dissolved Organic Nitrogen (DON) and Dissolved Organic Carbon (DOC) in Soil. Soil Biology and Biochemistry 2006, 38 (5), 991–999. <u>https://doi.org/10.1016/j.soilbio.2005.08.012</u>.
- (2) Agarwal, T.; Bucheli, T. D. Adaptation, Validation and Application of the Chemo-Thermal Oxidation Method to Quantify Black Carbon in Soils. *Environmental Pollution* **2011**, *159* (2), 532–538. <u>https://doi.org/10.1016/j.envpol.2010.10.012</u>.
- (3) Hale, S.; Hanley, K.; Lehmann, J.; Zimmerman, A.; Cornelissen, G. Effects of Chemical, Biological, and Physical Aging As Well As Soil Addition on the Sorption of Pyrene to Activated Carbon and Biochar. *Environmental Science & Technology* 2011, 45 (24), 10445–10453. <u>https://doi.org/10.1021/es202970x</u>.
- (4) Hawthorne, S. B.; Jonker, M. T. O.; van der Heijden, S. A.; Grabanski, C. B.; Azzolina, N. A.; Miller, D. J. Measuring Picogram per Liter Concentrations of Freely Dissolved Parent and Alkyl PAHs (PAH-34), Using Passive Sampling with Polyoxymethylene. *Anal. Chem.* 2011, 83 (17), 6754–6761. https://doi.org/10.1021/ac201411v.
- (5) Brändli, R. C.; Bucheli, T. D.; Kupper, T.; Stadelmann, F. X.; Tarradellas, J. Optimised Accelerated Solvent Extraction of PCBs and PAHs from Compost. *International Journal of Environmental Analytical Chemistry* 2006, 86 (7), 505–525. https://doi.org/10.1080/03067310500410839.