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Bioaccessibility of polycyclic aromatic hydrocarbons in activated carbon or biochar amended vegetated (*Salix viminalis*) soil[☆]

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A B S T R A C T

The aim of the present study was to determine the effect of activated carbon (AC) or biochars on the bioaccessibility (C_{bioacc}) of polycyclic aromatic hydrocarbons (PAHs) in soils vegetated with willow (*Salix viminalis*). The study determined the effect of willow on the C_{bioacc} PAHs and the effect of the investigated amendments on changes in dissolved organic carbon (DOC), crop yield and the content of PAHs in plants. PAH-contaminated soil was amended with 2.5 wt% AC or biochar. Samples from individual plots with and without plants were collected at the beginning of the experiment and after 3, 6, 12 and 18 months. The C_{bioacc} PAHs were determined using sorptive bioaccessibility extraction (SBE) (silicon rods and hydroxypropyl-β-cyclodextrin). Both AC and biochar caused a decrease in the C_{bioacc} PAHs. Immediately after adding AC, straw-derived biochar or willow-derived biochar to the soil, the reduction in the sum of 16 (Σ16) C_{bioacc} PAHs was 70.3, 38.0, and 29.3%, respectively. The highest reduction of C_{bioacc} was observed for 5- and 6-ring PAHs (from 54.4 to 100%), whereas 2-ring PAHs were reduced only 8.0–25.4%. The reduction of C_{bioacc} PAHs increased over time. Plants reduced C_{bioacc} in all soils although effects varied by soil treatment and PAH. Willow grown in AC- and biochar-amended soil accumulated less phenanthrene than in the control soil. The presence of AC in the soil also affected willow yield and shoot length and DOC was reduced from 53.5 to 66.9% relative to unamended soils. In the biochars-amended soil, no changes in soil DOC content were noted nor effects on willow shoot length.

1. Introduction

Soil contamination is a serious problem because it can lead to the accumulation of contaminants in plants and subsequently in the human food chain. Various methods of soil remediation have been used(de Boer and Wagelmans, 2016). However, conventional methods are costly and significantly interfere with the natural environment. The use of activated carbon (AC) has attracted great interest in recent years (Ghosh et al., 2011; Kupryianchyk et al., 2015) due to the strong affinity of contaminants for AC (Ghosh et al., 2011; Rakowska et al., 2014) and the resulting binding of the bioavailable/bioaccessible fraction of contaminants (Ghosh et al., 2011; Millward et al., 2005; Reible, 2014; Stringer et al., 2014). A significant reduction of bioaccessible contaminants in sediments contaminated with PAHs, PCB, mercury, methylmercury, PCDD/F and DDT was obtained by applying AC (Ghosh et al., 2011; Gomez-Eyles et al., 2013; Patmont et al., 2015; Samuelsson et al., 2015; Tomaszewski et al., 2008; Werner et al., 2005; Zimmerman et al., 2004). The binding of the bioaccessible fraction was often associated with a simultaneous reduction in the accumulation of these contaminants by various aquatic organisms (McLeod et al., 2007; Millward et al., 2005; Samuelsson et al., 2015; Tomaszewski et al., 2008). To date, research has been mainly focused on sediments and few studies of this type relate to soils (Brändli et al., 2008; Jakob et al., 2012; Kupryianchyk et al., 2016b; Oen et al., 2012) which have a different specificity and different properties than sediments. Studies on soil at field scale are relatively few (Hale et al., 2012a) and are typically of short duration.

Biochar is another adsorbent that could be an alternative to AC (Ahmad et al., 2014). Biochar has a smaller surface area than AC and its efficiency in binding organic contaminants (polycyclic aromatic hydrocarbons, polychlorinated biphenyls, etc.) is also smaller

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(Kupryianchyk et al., 2016b). However, biochar has many advantages. Biochar is cheaper comparing to AC. Conversion of biomass to biochar and its use for soil amendment have been proposed as one of the best methods of climate change mitigation through soil carbon sequestration (Lehmann, 2007). Moreover, biochar can be obtained from waste biomass or other waste products. Biochar contains many nutrients, which contributes to an improvement in soil properties and crop yields (Hussain et al., 2016). These advantages are particularly important when it is planned to grow crops in a rehabilitated area. In this case, the fertilizing advantages of biochar can be of great importance. The cultivation of plants (e.g. energy crops) can also aid remediation. The effect of plants on PAH degradation (phytoremediation) has been well described in the literature (de Boer and Wagelmans, 2016). It is known that root exudates can be a factor stimulating the growth of organisms capable of degrading PAHs.

The aim of the present study was to evaluate the efficiency of binding of the bioaccessible (C_{bioacc}) fraction of PAHs in soil contaminated with these compounds under natural conditions. The study also evaluated the effect of AC and biochar on changes in the content of soil dissolved organic matter (DOC), crop yield and PAH accumulation in willow as a secondary effect of amendment. The effect of willow on the content of C_{bioacc} PAHs in AC- or biochar-remediated soil was also evaluated.

2. Materials and methods

2.1. Adsorbents

The biochar used in the experiment was a commercial biochar provided by Fluid SA company (Poland) obtained from dried willow (*Salix viminalis*) (BCW) through a slow pyrolysis process in temperature range 600–700 °C. The second biochar was produced from wheat straw in temperature range 600–700 °C. This biochar was provided by MOSTOSTAL company (Poland). Activated carbon (AC) was purchased from POCH company (CAS: 7440-44-0, Poland). The physico-chemical properties of AC and biochars are presented in Table 1 and the methods of its determination in supporting information (SI).

2.2. Field experiment

The field experiment was performed nearby Chełm, Lubelskie, Poland (51°11′49.7″N 23°15′01.2″E). The experiment consisted of 7 plots (all plots were prepared in duplicates). The contaminated soil (Table 2) was transported from Dąbrowa Górnicza, Silesia, Poland and was associated with a Coking facility. The soil was homogenized and put in 2 m (w) x 2 m (l) x 0.2 m (d) plots. The study employed four mesocosms: (1) control (without any amendments), (2) treatment with biochar – BCW, (3) treatment with biochar – BCS and (4) treatment with activated carbon (AC). Particular amendments were added to the soil once in 2014 with the quantity of amendment corresponding to 50 t/ha (2.5 dry wt % of soil). The biochar dose was chosen as a most effective one based on previous study referred to the PAHs reduction in soils by biochars (Kołtowski et al., 2016b). Willow was planted on such prepared plots. Additionally, to evaluate the effect of plants on the content of C_{bioacc} PAHs, an experiment without plants (three additional mesocosms) was carried out concurrently to the experiment with willow. The unplanted experiment concerned only control and AC and BCW amendments. Soil samples were sampled five times from 2014 to 2015 (April 2014, July 2014, October 2014, April 2015, October 2015). Control soil (non-amended) and AC or biochar-amended soil samples were collected from the level of 0–20 cm with a (5–60 cm i.d.) stainless steel corer. Six independent samples (pseudo-replicates) were taken from each plot. The samples were transported to the laboratory, air dried in air- conditioned storage rooms (about 25 °C) for several weeks (in darkness), manually crushed, and sieved (<2 mm) prior to chemical analyses. After harvesting in October 2015 the willow shoots were thoroughly rinsed with water to remove soil and AC or biochar particles. Plant samples were air-dried at 25 °C and were ground to one sample and stored at −18 °C prior to analysis.

2.3. Bioaccessible (C_{bioacc}) PAH content

Bioaccessible concentration (C_{bioacc}) of PAHs was determined using silicon rods according to Gouliarmou and Mayer (2012). The silicon rods were cleaned before use by Soxhlet extraction with ethyl acetate for 100 h. Hydroxylpropyl-β-cyclodextrin (HPCD) solution was prepared by adding 75 g of HPCD and 200 mg of NaN_3 in 1 L of mili-Q water. Clean and dry silicone rods (length = 3 m) were placed in empty 100 mL Pyrex bottles. Then 100 mg of sample (soil or soil-biochar mixtures) and 50 mL of HPCD-solution were added to each bottle. Next, the samples were shaken in horizontal, orbital shaker at >200 rpm at room temperature for 30 d. HPCD were used a diffusive carrier to enhance desorption of PAHs from the matrix. The silicon rod continuously absorbs contaminants from the HPCD solution, effectively measuring both freely dissolved and reversibly bound PAHs, which together are defined as the bioaccessible fraction. Recovery standards were spiked and extraction was carried out using 2 × 100 mL of acetone without shaking once for 6 h and once overnight. The acetone extracts were combined and concentrated to 1 mL.

2.4. Gas chromatography – mass spectroscopy (GC-MS)

A qualitative and quantitative analysis of PAHs was carried out 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 select ion monitoring mode. A Rxi®-5 ms crossbond® 5% diphenyl and 95% dimethyl polysiloxane fused capillary column (30 m × 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 mL min^{-1}. The detection was performed with a Thermo Scientific ISQ LT mass spectrometer in the electron impact mode with a −70 eV ionisation energy and a dwelling time of 22 milli-seconds.

Table 1
Properties of adsorbents used in the experiment.

Biochar	pH	C	H	N	O	Ash	H/C	O/C	(O+N)/C	S_{BET}	S_{mic}	V_p	V_{mic}	Σ16 PAHs
AC	6.0	85.50	0.27	0.62	3.45	10.16	0.038	0.03	0.036	617.6	306.7	0.374	0.148	0.9
BCW	9.1	52.20	2.23	1.13	25.15	19.07	0.043	0.273	0.380	5.3	4.1	0.009	0.002	4.6
BCS	9.9	53.87	1.76	0.91	2.32	41.15	0.039	0.032	0.046	26.3	10.8	0.026	0.005	19.9

pH: reactivity in KCl; C, H, N, O: elemental composition [%]; Ash: ash content [%]; H/C, O/C and (O+N)/C – molar ratios; S_{BET}: surface area [m^2/g]; S_{mic}: micropore area [m^2/g]; V_p: total pore volume [cm^3/g]; V_{mic}: micropores volume [cm^3/g]; R: average pore radious [nm]; Σ16 PAHs: sum of total content of 16 PAHs [mg/kg]; Σ16 C_{free}: sum of freely dissolved 16 PAHs [ng/L].