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The concentration and changes in freely dissolved polycyclic aromatic hydrocarbons in biochar-amended soil☆

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ABSTRACT

The presence of polycyclic aromatic hydrocarbons (PAHs) in biochars hinders their environmental use. The aim of this study was to determine the freely dissolved (C_{free}) PAH content in soil amended with biochar in a long-term (851 days) field experiment. Biochar was added to the soil at a rate of 30 and 45 t/ha. The addition of biochar to the soil resulted in a decrease in Σ13 C_{free} PAHs by 25 and 22%, in the soil with the addition of biochar at the rate of 30 and 45 t/ha, respectively. As far as individual PAHs are concerned, in most cases a reduction in C_{free} was also observed (from 3.6 to 66%, depending on the biochar rate). During the first 105 days of the experiment, the content of Σ13 C_{free} in the biochar-amended soil significantly decreased by 26% (30 t/ha) and 36% (45 t/ha). After this period of time until the end of the experiment, no significant changes in C_{free} were observed, regardless of the biochar rate. However, the behavior of individual PAH groups differed depending on the number of rings and experimental treatment. Ultimately, after 851 days of the experiment the content of Σ13 C_{free} PAHs was lower by 29% (30 t/ha) and 35% (45 t/ha) compared to the beginning of the study as well as lower by 40% (30 t/ha) and 42% (45 t/ha) than in the control soil. The log K_{TOC} coefficients calculated for the biochar-amended soils were higher immediately after adding biochar and subsequently they gradually decreased, indicating the reduced strength of the interaction between biochar and the studied PAHs. The obtained results show that the addition of biochar to soil does not create a risk in terms of the content of C_{free} PAHs.

1. Introduction

The use of biochar in agriculture is becoming increasingly more common (Gurwick et al., 2013). In the past years amendment of contaminated soil with biochar has received more attention. Numerous studies have shown that biochar besides of contaminants immobilization, improves chemical, physical and biological soil properties. However, biochars can contain numerous organic and inorganic contaminants (Hale et al., 2012; Hilber et al., 2012; Oleszczuk et al., 2013; Qiu et al., 2015; Yargicoglu et al., 2015). While the content of inorganic contaminants largely depends on the quality of feedstock used to produce the biochar, the presence of organic contaminants is associated in most cases with biochar formation conditions (Zielińska and Oleszczuk, 2015a). Heavy metal contents in biochars can be reduced by selecting a proper material for its production. The situation is worse in the case of contaminants, such as PAHs formed during biochar production. These compounds are of particular concern due to their mutagenic and carcinogenic properties. PAH contents determined in biochars can range widely from 0.1 to even 10,000 mg/kg (Freddo et al., 2012; Hilber et al., 2012; Oleszczuk et al., 2013; Bucheli et al., 2015). Existing legislation in Germany (Federal Soil Protection Act) and Switzerland (Chemical Risk Reduction Act) (Hans-Peter Schmidt, 2013) distinguishes two major categories of biochar depending on the contaminant content. One category is basic grade biochar (sum of 16 PAHs < 12 mg/kg). The other category is premium grade biochar (sum of 16 PAHs < 4 mg/kg). The standards for basic grade biochar are almost 50% higher than for sewage sludge; the standards for the sum of nine PAHs have been set at 6 mg/kg

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(EU, 2000). The supporters of biochar use argue that the high content of these compounds in biochars does not pose any risk since the compounds are strongly bound by the biochar matrix. One study reported (Hale et al., 2012) only a trace (background) level of freely dissolved (C_{free}) PAH content i.e., the bioavailable fraction in biochars. The determined content of C_{free} PAHs was much lower than that observed for uncontaminated sediments. Our previous study (Zielińska and Oleszczuk, 2016) also demonstrated that a content of C_{free} PAHs in sewage sludge-derived biochars was markedly lower than the content in the corresponding sewage sludge. Thus far, this has been the only study on the potentially bioavailable fraction in biochars despite the urgency of this topic due to the common use of biochars. The opponents of biochar use argue that, even though PAHs are strongly bound to the biochar, with aging of biochar the strength of the biochar-PAH interactions will decrease, resulting in the release of PAHs into the environment. No information has been published to confirm or reject this possibility.

Published research has mainly focused on the immobilization of organic and inorganic contaminants in soils contaminated with these compounds using biochars (Mohan et al., 2014). Only three studies have investigated the changes in PAH content in biochar-amended soils (Kuśmierz et al., 2016; Quilliam et al., 2013; Rombolà et al., 2015); these studies did not consider the content of C_{free} PAHs. Addition of biochar to PAH-contaminated soil significantly reduces the bioavailability of PAHs (Khan et al., 2015) and the bioaccumulation of PAHs from soil contaminated by these compounds by turnip (*Brassica rapa* L.) (Khan et al., 2015), tomato (*Solanum lycopersicum*) (Waqas et al., 2015) and lettuce (*Cucumis sativa* L.) (Waqas et al., 2014). But, there is no information in the literature on the bioavailability of biochar-derived PAHs. The two studies that have been published show that PAHs present in the added biochar undergo various processes in the soil (Kuśmierz et al., 2016; Quilliam et al., 2013). Similarly, as in soils amended with other PAH-containing materials (e.g. sewage sludge), in the case of biochar-amended soils, these compounds can also biodegrade, leach or evaporate (Oleszczuk, 2006). Nevertheless, due to the high affinity of biochar for PAHs (Devi and Saroha, 2015; Zielińska and Oleszczuk, 2015b), these processes can be significantly reduced, which may increasing the persistence of PAHs in the soil by reducing their bioavailability. Given the increasing use of biochar, it is important to determine the persistence of PAHs in soils, particularly concerning their bioavailability.

The aim of this study was to determine the content of freely dissolved (C_{free}) PAHs after soil amendment with biochar and to monitor the temporal change in content of C_{free} depending on the biochar dose. C_{free} content corresponds to the bioavailable fraction of hydrophobic organic compounds, namely the fraction available to organisms. Based on the obtained results, K_{TOC} values were determined for biochar-amended soils. This allowed determination of the change (or absence) in the interactions between biochar-amended soil and PAHs. The percentage of C_{free} in the total PAH content and its change over time were also determined.

2. Materials and methods

2.1. Field experiment

Biochar and soil properties are presented in supplemental information (Tables S1 and S2). Biochar was obtained commercially (Mostostal Sp. zo.o., Wrocław, Poland). The product had been produced by pyrolysis in an industrial furnace from wheat straw at temperatures ranging from 350 °C (start of pyrolysis) to 650 °C (max. pyrolysis temperature) in an oxygen-poor atmosphere (1–2% O_2).

A field experiment was carried out from 2011 to 2013, at the Bezek Experimental Station (Poland). The experimental field was located on incomplete Podzolic soil lying on marl substrate with the granulometric composition of loamy sand.

A randomized experiment with three replicates was carried out in three experimental variants (15 m^2 each). The biochar was introduced in the following doses: soil without fertilization – control (0 t/ha), 30 t/ha and 45 t/ha. The biochar was introduced into soil once on April 2011. Biochar doses were calculated taking into consideration the biochar's dry mass and the density of the solid soil phase. Biochar was spread out by hand on the plots and mixed into the soil with a cultivator and plough (10 cm deep). Control treatments were ploughed the same way as the experiment with biochar. Thereafter, barley (*Hordeum sativum* L.) was sown at the first year of the experiment and oat (*Avena sativa* L.) at the second year of the experiment. The biochar doses were chosen so that the theoretically calculated concentration of total PAHs in surface soil layer (up to 10 cm) after biochar application would not exceed 1 μg/g, i.e. the highest permissible level under the Polish law concerning PAHs content in soils.

2.2. Sample collection and preparation

Soil samples for the analyses were collected from the experimental plots exactly after the application of biochar, and then after 21, 105, 474 and 851 days. Surface (0–10 cm) soil and biochar-amended samples were collected with a (5 cm i. d. x 60 cm) stainless steel corer. Ten independent samples (replicates) were taken from each plot and were mixed to obtain a representative sample. After transport to the laboratory the samples were dried in dark, in the air atmosphere at temperature of 20–23 °C. Before the chemical analysis, soil samples were crushed and sieved through a sieve with mesh size of 2 mm.

2.3. Freely dissolved (C_{free}) PAH determination in biochars-amended soil

For freely dissolved PAH determination dry samples (1 g) 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 (200 mg L^{-1}) in order to eliminate any possible effect of remaining microorganisms and strips of 76-μm thick polyoxymethylene (POM) passive samplers (about 0.35 g for all batches) were added to vials (all carried out in triplicates). Prior to use, POM samplers were cleaned one day in methanol, then one in heptane, rinsing thoroughly with Millipore water and finally drying. Flasks were rolled end over end for 1 month at 1 RCF. During this time, an equilibrium between the sampler and the water is reached and the bioavailable pollutant concentration can be obtained (Jonker and Koelmans, 2001). After 30 days 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) and spiked with TTB as an internal standard for quantification via GC/MS. A qualitative and quantitative analysis of PAHs was carried out in the same way as in the case of total PAH analysis. The concentration of PAH on POM passive samplers (C_{POM}) was calculated according to the equation (1):

$$C_{POM}\left(ng\ kg^{-1}\right) = \frac{m_{PAH}\ (ng)}{m_{2POM}\ (kg)} \quad (1)$$

where m_{PAH} (ng) is the mass of PAH determined via GC/MS and