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Changes of total and freely dissolved polycyclic aromatic hydrocarbons and toxicity of biochars treated with various aging processes☆

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ABSTRACT

The aim of this study was to determine the effect of biochar aging on the content of polycyclic aromatic hydrocarbons (PAHs) (the total content – C_{tot}, and the freely dissolved – C_{free}) in biochar and its ecotoxicity. Two biochars (BCS and BCM) with varying properties were aged for 420 days at different temperatures (−20 °C, 4 °C, 20 °C, 70 °C), at a variable temperature (−20/20 °C), in the presence of nutrients, and in the presence of inoculum and nutrients. After the aging process, C_{tot} and C_{free} PAHs were determined in samples obtained and an ecotoxicological analysis was performed, which involved tests with bacteria (*Vibrio fischeri*), invertebrates (*Folsomia candida*) and plants (*Lepidium sativum*). Aging significantly affected all the parameters tested. The range of changes in the studied parameters depended on the type of biochar and ageing conditions. In the case of most of the aging methods, PAH content (C_{tot}, C_{free}) and toxicity were found to decrease. Aging in the presence of microorganisms and nutrients and in the presence of nutrients alone caused the greatest reduction in C_{tot} PAH content (a reduction from 30 to 100% relative to non-aged biochar), C_{free} PAH content (a reduction from 12 to 100%), root growth inhibition (a reduction from 73 to 90%), and luminescence inhibition (a reduction from 24 to 100%). In the case of C_{free} PAHs and toxicity to *F. candida*, some aging methods caused their increase. The study also found a significant relationship between the changes in C_{tot} PAH content during aging and inhibition of root growth (BCS, BCM) and inhibition of *V. fischerii* luminescence (BCM). In no case was a significant correlation ($P \geq 0.05$) between C_{free} PAHs and the investigated toxicity parameters found.

1. Introduction

The use of biochar in different applications related to fertilization and soil rehabilitation and remediation is becoming more and more common (Cha et al., 2016). Nevertheless, the content of organic contaminants in biochar, with polycyclic aromatic hydrocarbons (PAHs) being a significant group of such contaminants, can be a limitation for biochar application, in particular if it is used to improve soil properties (Hale et al., 2012; Oleszczuk et al., 2013). Due to their mutagenic, cancerogenic and toxic properties, PAHs are considered to be contaminants that require special attention. This is particularly important in the case of fertilizer materials which, when applied to soils, can increase the content of these compounds in the soil. This may lead to the accumulation of PAHs in plants and subsequently to their incorporation into the human food chain. While there is intensive research on the effect of pyrolysis on the content and bioavailability of PAHs contained in biochar (Hale et al., 2012; Qiu et al., 2015; Stefaniuk et al., 2016; Zielińska and Oleszczuk, 2015, 2016), in the literature there is a lack of information on the persistence and bioavailability of PAHs in biochar that undergoes aging processes under various conditions (Kołtowski and Oleszczuk, 2015a; Sigmund et al., 2017). It is known that with time biochar undergoes various processes that result in changes in its properties, the so-called aging (Cheng et al., 2006; Nguyen and Lehmann, 2009; Bakshi et al., 2016; Sorrenti et al., 2016). Slow biochar aging in soils and sediments occurs through (Nguyen and Lehmann, 2009) microbial degradation and/or abiotic oxidation. However, changes in individual properties are largely determined by the type of biochar, pyrolysis temperature and aging conditions. CEC and biochar polarity usually increase (Cheng et al.,

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2006; Nguyen and Lehmann, 2009). At the same time, biochar pH and hydrophobicity decrease (Bakshi et al., 2016; Ghaffar and Abbas, 2016; Zhang et al., 2016). As far as the surface area is concerned, there are divergent data that show either an increase or a decrease in surface area (Heitkötter and Marschner, 2015; Bakshi et al., 2016). The structural properties of biochar also undergo changes (Liu et al., 2013). All such changes influence the interaction strength between contaminants and biochar. In the case of hydrophobic compounds, the strength of their interaction with biochar usually weakens as a result of the above processes (Hale et al., 2011; Kumari et al., 2014; Ghaffar and Abbas, 2016; Zhang et al., 2016). However, the above-mentioned studies mainly relate to externally introduced compounds. But in the literature there is a lack of information on how the process of biochar aging affects the interactions between compounds contained in the biochar and the changing biochar, and how this process influences the toxicity of such biochar. It is generally accepted (Hale et al., 2012) that PAHs are permanently bound to biochar and their availability to organisms is marginal; therefore, they do not pose a threat. Nevertheless, these are theoretical assumptions that have not been experimentally confirmed. But our recent study revealed that in a biochar-amended soil PAHs are degraded (Kuśmierz et al., 2016) and can stimulate the degradation of PAHs in a sewage sludge-amended soil (Stefaniuk et al., 2017). Up to now, Sigmund et al. (2017) investigated the influence of ageing on biochar properties using H_2O_2 thermal oxidation or horseradish peroxidase enzymatic oxidation. Concentrations of the 16 US EPA PAHs were measured in all of the biochars and a contaminant trap was used to investigate the effect of ageing on their bioaccessibility. The total and bioaccessible PAH concentrations decreased for both artificially and field-aged biochars, indicating that biochars release PAHs when they are freshly produced and that the risk of PAH release decreases with ageing.

The changes that biochar undergoes, which have been confirmed in numerous studies (Cheng et al., 2006; Cheng and Lehmann, 2009; Liu et al., 2013; Kumari et al., 2014), allow to presume that under the influence of aging they will affect the content and bioaccessibility of PAHs. The very changes in biochar properties may also affect biochar toxicity. The absence of biochar toxicity, which is associated with the presence of PAHs, is usually attributable to the strong binding of PAHs by the biochar (Hale et al., 2012). Thus, a weakening of these bonds due to aging may potentially increase biochar toxicity. On the other hand, however, a weakening of the biochar-PAH bond may increase the bioavailability/bioaccessibility of PAHs and their susceptibility to degradation. Thus far, these issues have not been undertaken.

The aim of the present study was to determine how different biochar aging processes affect the total PAH content (C_{tot}) and the content of freely dissolved PAHs (C_{free}) (which represent the mobile fraction) in the context of biochar properties and toxicity in relation to three different groups of organisms commonly used in ecotoxicological tests. For the purpose of comparison, two biochars with varying properties but with a similar content of C_{tot} PAHs were used.

2. Materials and methods

2.1. Biochar aging process

Two biochars were selected for testing: biochar derived from wheat straw (BCS) and biochar derived from elephant grass (Miscanthus) (BCM). The aim was to compare the PAHs content depending on feedstock used for biochar production. The biochars investigated here were obtained from commercial manufacturer and were produced by pyrolysis of feedstock at a temperature 650 °C in an oxygen-poor atmosphere (<1%). Biochar BCS was provided by Mostostal Sp. z o.o. (Wrocław, Poland) and biochar BCM was provided by Fluid S.A. (Sędziszów, Poland). Artificial aging was carried out in the laboratory over fourteen months. According to the nomenclature adopted by Hale et al. (2011), the following three aging regimes were used; chemical (treatment at −20, 4, 20, 70 °C), biological (nutrient solution, nutrient solution + biological inoculum), and physical (changing temperature 20/-20 °C). These are the methods most frequently used in research on artificial aging of biochar (Cheng et al., 2006; Cheng and Lehmann, 2009; Nguyen and Lehmann, 2009; Hale et al., 2011) which are designed to accelerate the aging of biochar under natural conditions.

Chemical aging was carried out by continually exposing the dry biochars (30 g) to −20, 4, 20 and 70 °C in airtight stainless steel containers, which are referred to as BCS-20/BCM-20, BCS4/BCM4, BCS20/BCM20 and BCS70/BCM70 respectively, throughout the manuscript.

Biological aging consisted of exposing the biochars (30 g) to a microbial inoculum (3 mL) and nutrient solution (1.5 mL) (6.38 g/L glucose, 40.66 g/L NH_4Cl, 4.67 g/L KH_2PO_4, 10.00 mg/L peptone, 24.00 mg/L $CaCl_2$, 4.00 mg/L $MnSO_4$, 4.00 mg/L $ZnCl_2$, 4.00 mg/L $CuSO_4$, 16.00 mg/L $MgCl_2$ and a glucose supplement − 40 μg/mg BC) (BCS-M/BCM-M), similar to previous studies (Hale et al., 2011) or only to same nutrient solution (BCS-N/BCM-N). The microbial inoculum was extracted from a PAH contaminated soil sampled from a coking plant area (Dabrowa Gornicza, Poland) (Kołtowski et al., 2016). The soil was incubated at 30 °C for 18 days to stimulate the microbial community prior to obtaining the inoculum. Soil and Millipore water were mixed and rolled end-over end (11 rpm; 2 h) and then filtered (2.7 μm) to obtain the inoculum (Hale et al., 2011). The ratio of inoculum to nutrient solution was 2:1 according to suggestion of Heitkötter and Marschner (2015).

During physical aging, biochar (30 g) was subjected to freeze thaw cycles between −20 °C (7 days) and +20 °C (7 days) and physical aged biochar is referred to as BCS-P/BCM-P.

Each experiment was conducted in 3 replicates. After a period of 14 months, samples subjected to aging were dried and further analyzed.

2.2. Total (C_{tot}) and freely dissolved (C_{free}) PAHs content determination

Total concentration of PAH was determined by extracting samples with hexane in Soxhlet apparatus. Then, the extract from biochar were subjected to the clean-up procedure (liquid-liquid partitioning and open glass column filled with activated silica gel) according to (Bucheli et al., 2004). After the clean-up the extracts were concentrated and analyzed by GC-MS.

C_{free} concentration of PAH was determined as described previously (Cornelissen et al., 2008). Brefly, the polyoxymethylene (POM) strips (about 0.35 g) were put into a conical flask containing 1 g dry weight (dw) of biochar and 40 mL of Milli-Q water with 0.2 g/L NaN_3 to inhibit microbiological growth. The samples were mixed for 30 days. Then, the strips were removed, cleaned in Milli-Q water and dried and extracted with 20 mL acetone/heptane (20:80 v/v). After 48 h of horizontal shaking the samples were concentrated to 1 mL and analyzed by GC-MS. Detailed information about C_{tot} and C_{free} PAHs determination and calculation and information about statistical analysis are presented in Supporting information.

2.3. Toxicity determination

Samples were evaluated by two solid (Phytotoxkit F, Collembolan test) and two liquid phase tests (Microtox®, Phytotestkit F). To evaluate biochar toxicity to springtails, the test was carried out