Bioavailability and bioaccessibility of polycyclic aromatic hydrocarbons from (post-pyrolytically treated) biochars

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HIGHLIGHTS

- Desorption resistance of PAHs in biochar was determined with contaminant traps.
- PAHs in biochar were mostly desorption resistant.
- Where observed, bioaccessibility of PAHs in biochar was concentration independent.
- Exposure of PAHs in biochar becomes relevant at high concentrations (>10 mg/kg$_{dw}$).
- Biochars acted more as a sink than a source for PAHs.

GRAPHICAL ABSTRACT
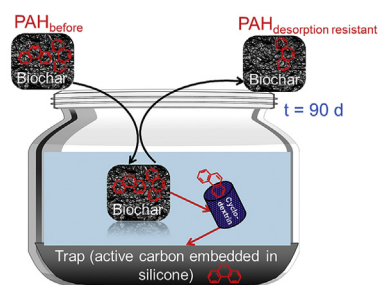
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ABSTRACT

Bioaccessibility data of PAHs from biochar produced under real world conditions is scarce and the influence of feedstock and various post-pyrolysis treatments common in agriculture, such as co-composting or lacto-fermentation to produce silage fodder, on their bioavailability and bioaccessibility has hardly been studied. The total (C_{total}), and freely dissolved (i.e., bioavailable) concentrations (C_{free}) of the sum of 16 US EPA PAHs of 43 biochar samples produced and treated in such ways ranged from 0.4 to almost 2000 mg/kg, and from 12 to 81 ng/L, respectively, which resulted in very high biochar-water partition coefficients ($4.2 \leq \log K_D \leq 8.8$ L/kg) for individual PAHs. Thirty three samples were incubated in contaminant traps that combined a diffusive carrier and a sorptive sink. Incubations yielded samples only containing desorption-resistant PAHs (C_{res}). The desorption resistant PAH fraction was dominant, since only eight out of 33 biochar samples showed statistically significant bioaccessible fractions ($f_{bioaccessible} = 1 - C_{res}/C_{total}$). Bioavailability correlated positively with C_{total}/surface area. Other relationships of bioavailability and –accessibility with the investigated post-pyrolysis processes or elemental composition could not be found. PAH exposure was very limited (low C_{free}, high C_{res}) for all samples with low to moderate C_{total}, whereas higher exposure was determined in some biochars with $C_{total} > 10$ mg/kg.

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1. Introduction

Biochar can contain considerable amounts of polycyclic aromatic hydrocarbons (PAHs) produced during the pyrolysis process. Concentrations of PAHs range from a few to a few 100 mg/kg for the sum ($\sum$) of the 16 US environmental protection agency's (EPA) priority PAHs (Bucheli et al., 2015). In agriculture, biochar is often blended with mineral or organic fertilizers to increase its effect on soil fertility and crop yield (Atkinson et al., 2010; Sohi et al., 2010). In animal farming, the amendment of biochar into feed of ruminants is intended to reduce greenhouse gas emissions or improve the feed quality (Hansen et al., 2012; Silivong and Preston, 2015). To reduce nutrient losses during composting, biochars can be added to composting biomass (Khan et al., 2014). Biochar is also used to remediate contaminated soils and sediments by organic pollutants (Hale et al., 2015; Denyes et al., 2016).

While total concentrations (C_{total}) of pollutants such as PAHs are currently applied in legislation for the agricultural use of biochar (Bucheli et al., 2015), the C_{total} can significantly overestimate the actual risk of organic contaminants (Verstraete and Devliegher, 1996), particularly in cases where the pollutants themselves are strongly sorbed to the matrix (i.e., high partition coefficients) and where they are not readily desorbed from the matrix (i.e., high desorption resistant fraction). Actual exposure can be assessed by the chemical activity (i.e. expressed as freely dissolved concentration) and the bioaccessibility (i.e., readily desorbing fraction) (Reichenberg and Mayer, 2006). Freely dissolved (i.e., bioavailable) concentrations of native PAHs in soils or biochars (C_{free}) were earlier measured by, e.g., Hale et al. (2012), with non-depletive equilibrium sampling methods. Bioaccessibility can be measured with depletive sampling methods such as Tenax® (Hilber et al., 2009; Cui et al., 2013) or Sorptive Bioaccessibility Extraction (Gouliarmou and Mayer, 2012). These bioaccessibility techniques have recently been extended to samples with very high sorption capacities for PAHs, such as historically polluted soil or chimney soot (Gouliarmou and Mayer, 2012; Gouliarmou et al., 2013), but were unable to determine bioaccessible fractions ($f_{bioaccessible}$) for biochar (Mayer et al., 2016). As conceptually shown in Mayer et al. (2016), so far, $f_{bioaccessible}$ of PAHs from biochar can only be determined indirectly as one minus the ratio of desorption resistant PAH concentration (C_{res}) to C_{total}. The C_{res} can be quantified after incubation of biochars in contaminant traps, where cyclodextrin serves as diffusive carrier, and an active carbon (AC)/silicone composite as an infinite sink that maintains the desorption gradient (Mayer et al., 2011). This method is particularly suitable for matrices that have very high partition coefficients for organic contaminants (Mayer et al., 2016).

The aim of this study was to determine the bioavailability and −accessibility of native PAHs in biochars gathered from various producers in the field, both in pure form or after subjection to various post-pyrolysis treatments common in agriculture, or with biochar producers. The scientific hypothesis was that such treatments, potentially manifested in an altered biochar elemental composition and/or specific surface area, increase bioavailability and −accessibility of PAHs. For treatments involving microbial processes (e.g., composting, lacto-fermentation) in particular, this hypothesis is motivated by findings that microbes may promote desorption and degradation of PAHs sorbed to carbonaceous materials (Xia et al., 2010), and that degradation of PAHs by biofilm-producing bacteria was improved in presence of activated carbon (Leglize et al., 2008). To this end, physical-chemical properties, as well as PAH bioavailability and -accessibility were quantified in a set of diverse biochars, (some of) which were i) produced by different biochar providers from commonly used feedstock material, ii) pyrolysed under a 2% oxygen (O_2) atmosphere to simulate non-controlled pyrolysis conditions, iii) mixed and aged with compost to represent a common agricultural waste product with a drastically altered microenvironment, iv) subjected to lacto-fermentation because biochar is used as a feed additive and usually applied in combination with lacto-fermented feed-products (Hansen et al., 2012; Silivong and Preston, 2015), and v) treated post-pyrolytically with ozone, a process which may increase PAH bioaccessibility (Bernal-Martinez et al., 2007). Please note that this is a field, and common practice orientated experiment where bioavailability and −accessibility including physical-chemical biochar properties were surveyed, rather than a mechanistic lab study under controlled conditions. Still, this study sheds new and relevant light on the exposure assessment of biochar produced, and post-pyrolytically treated in the field. Due to the width and breadth of the investigated samples, the here presented results should be equally relevant for scientists, legislators, and biochar practitioners.

2. Material and methods

2.1. Samples

Table 1 provides details about the 43 biochar and four compost samples. The majority of the feedstocks of the biochar samples (24) consisted of "wood", with the remainder being divided as follows: two "sugar beet" samples, six "*Miscanthus*" (elephant grass), five "lop" (green waste) and six "miscellaneous" materials, e.g., grape pomace, coffee grounds, sewage sludge. The names in the quotation marks refer to the feedstock groups listed in Table 1, which also includes the feedstock of the composts specified in the supporting information (SI). All biochars were produced by slow pyrolysis by different professional and amateur biochar producers under field scale real world conditions at temperatures between 400 and 750 °C.

Table 1 also lists the treatment in the "sample description" and the group it belongs to in the "**treatment group**" (bold in the text). Biochars that were not treated or blended with other additives after pyrolysis are labeled "**pure**". Some of the biochars were blended with microorganisms such as lactobacilli and photosynthetic bacteria, yeasts, actinomycetes, and fungi, all commercially available at the agro-market (the product is described in detail in the SI). These samples are referred to as treatment group "**microorganisms**" and were fermented for 2 weeks at 35 °C following microorganism addition. Some biochars were mixed with biomass at different ratios and co-composted at the facilities of a commercial compost producer. These are labeled "**blend**". Corresponding pure composts are named "**compost**". The feedstock and composting process is described in detail in the SI. Furthermore, aliquots of the sieved coniferous wood residues, sugar beet, and elephant grass (*Miscanthus*) feedstocks were slowly pyrolysed under a 2% O_2 atmosphere and allocated to the **O_2** treatment group. The *Miscanthus* biochar was also treated with ozone after pyrolysis at 700 °C and was labeled **O_3**. Pure biochars in Table 1 were numbered consecutively and their respective treatments received a corresponding letter in alphabetic order. The last column in Table 1 defines the samples that were subjected to contaminant traps. Thirty three samples were selected for the trap experiments (see section 2.5) and these samples represented all six treatment groups as well as samples with high and low C_{total} from the **pure** treatment group.

The samples were stored and treated according to Hilber et al. (2012). Briefly, the samples were dried at 40 °C overnight, ground to ≤0.75 mm with a cutting mill SM1 Retsch GmbH (Haan, Germany) to reduce constitutional heterogeneity and allow for representative subsampling (Hilber et al., 2017), and mixed thoroughly