

Is biochar a source or sink for polycyclic aromatic hydrocarbon (PAH) compounds in agricultural soils?

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) in the environment originate mainly from incomplete combustion of fossil fuels, and pose a significant human health risk. Soils act as environmental sinks for PAHs, as they become strongly absorbed onto soil particles; degradation is mainly driven by microbial catabolism, although it is dependent on PAH bioavailability. There is current interest in burying biochar in soil as a long-term soil carbon store; however, biochar inherently contains varying levels of PAHs and its application could contaminate soil, and its high sorptive capacity may facilitate the persistence of PAHs in the environment. The aim of this study was to determine the effect of adding biochar to soil on microbial mineralization of PAHs, and to quantify whether or not soils amended with biochar were less likely to leach PAHs. We used contrasting agricultural soils (Eutric Cambisol and Cambic Podzol) spiked with the labelled PAH compound ^{14}C -phenanthrene and amended with either wood biochar or rice husk biochar. Mineralization was quantified by measuring the release of $^{14}\text{CO}_2$ and simulated rain used to quantify leaching of PAH through biochar-amended soil. Rice husk biochar had higher concentrations of PAHs (64.65 mg kg^{-1}) than wood biochar (9.56 mg kg^{-1}), and both soil types contained quantifiable levels of PAHs. However, soil that had contained biochar for 3 years had significantly higher levels of PAH (1.95 mg kg^{-1}) compared to unamended soil (1.13 mg kg^{-1}). PAH catabolism in soil was reduced when amended with biochar, although biochar amendment did not consistently decrease PAH leaching. Biochar-mediated inhibition of PAH mineralization is a consequence of increased sorption and reduced bioavailability. Before large scale biochar addition to soils is adopted, future work is needed to address the dynamic between sorbent saturation and microbial activity and how this relates to the concentration of PAHs in soil solution and their persistence in the environment.

Keywords: Black carbon, Carbon sequestration, Leaching, Microbial degradation, PAH persistence, PAH sorption and microbial activity, Soil pollution

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are classified as persistent organic pollutants commonly occurring in the environment and are considered to be one of the most difficult organic contaminants to treat (Edwards, 1983; Cerniglia, 1992; Weissenfels *et al.*, 1992; Zheng *et al.*, 2007). Due to their toxic, mutagenic and carcinogenic properties they pose a significant environmental risk to public health (Chen & Liao, 2006), with 16 PAHs being identified as priority pollutants by both the US Environment Protection Agency (USEPA) and the European Union (USEPA, 1977; European Union, Commission Recommendation, 2005). Although natural processes, such as volcanic eruptions and grassland and forest fires, give rise to PAHs (Kim

et al., 2003), the greatest source of PAH pollution in the environment results from past and present industrial processes such as the incomplete combustion of fossil fuels and the open burning of biomass (Khalili *et al.*, 1995; Simoneit, 2002; Lemieux *et al.*, 2004). The lipophilic structure of PAHs makes them extremely hydrophobic, making PAHs mainly contaminants of soil rather than water. Consequently, soils and sediments act as strong environmental sinks for PAHs as they become rapidly absorbed onto soil particles, in particular humic materials associated with soil organic matter (SOM) (Macleod & Semple, 2002).

Biochar is produced from the pyrolysis of organic materials, and when incorporated in soil can act as a long-term soil C store, i.e. remaining >100 years (Lehmann, 2007). Subsequently, amending soil with biochar is receiving increasing attention as an intervention strategy for the sequestration of C (Lehmann, 2007; Powlson *et al.*, 2011). In addition, biochar

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application can increase crop yields and reduce the leaching of nutrients from soil (Jeffery *et al.*, 2010; Singh *et al.*, 2010). However, during pyrolysis PAHs, dioxins and furans are produced which means that biochar inherently contains varying levels of these organic pollutants (Garcia-Perez, 2008; Hale *et al.*, 2012a). Therefore, the application of biochar to agricultural soil could carry a significant risk to human health by contaminating soils. Alternatively, as biochar can stimulate microbial activity in soil (Kolb *et al.*, 2009; Steinbeiss *et al.*, 2009; Quilliam *et al.*, 2012a) its addition could facilitate the degradation of naturally occurring PAHs. Microbial degradation of PAHs in soil is strongly influenced by a number of factors, including pH, soil type, aeration and nutrient and water availability, in addition to the physio-chemical properties of the PAH, its concentration in the soil, the presence of a microbial community capable of degrading PAHs and its relative bioavailability (Cerniglia, 1992; Kastner *et al.*, 1998; Breedveld & Sparrevik, 2000; Volkering & Breure, 2003; Zhang *et al.*, 2006; Ding *et al.*, 2010). As biochar is particularly effective at adsorbing and sequestering organic contaminants, enhanced sorption of hydrophobic organic compounds such as PAHs could actually decrease microbial mineralization by decreasing bioavailability (Rhodes *et al.*, 2008, 2010; Xia *et al.*, 2010), and could lead to localized PAH accumulation. However, the strong sorbing capacity of biochar could limit the leaching of PAHs from soils and could prove a significant management strategy for the reduction of PAH contamination of groundwater (Hale *et al.*, 2012b).

The environmental fates of biochar-associated PAHs added to soil are still poorly understood. Soil type can have a significant effect on PAH degradation, e.g. soils with a higher sorptive capacity due to higher levels of SOM can influence microbial catabolism by reducing mass transfer of PAHs in soil solution (Macleod & Semple, 2002). However, adsorption is non-linear, and therefore, with high levels of pollutant, sorbent saturation would result in more freely available PAHs, and could lead to increased levels of degradation (Cornelissen *et al.*, 2005; Rhodes *et al.*, 2010).

The aim of this study was to (i) quantify the concentration of the 16 priority PAHs in soil that has been amended with biochar for 3 years at two different rates, and (ii) determine the effect of adding biochar to two contrasting agricultural soils on microbial mineralization of PAHs and to quantify whether or not biochar-amended soil is less likely to leach PAHs following a simulated rain event. To address this we have used ¹⁴C-labelled phenanthrene (a common PAH compound) to quantify mineralization and leaching in two soils amended with two different types of biochar (made

from either wood or rice husk) contaminated with either a high or low level of phenanthrene. Phenanthrene is found in high concentrations in PAH contaminated environmental samples and subsequently is often used as a surrogate model compound for studying biodegradation and microbial mineralization of PAHs (Bezalel *et al.*, 1996).

Materials and methods

Biochar field site and soil and biochar analysis

An experimental biochar field trial, established in 2009 at Aber-gwynnregyn, Wales (53°14'N, 4°01'W), was used to determine the longer term (3 years) effects of adding biochar to the concentration of PAH in the soil. The soil is classified as a Eutric Cambisol, has a sandy clay loam texture and is derived from mixed glacial till of Ordovician origin deposited approximately 10 000 years ago. Replicate ($n = 4$) plots (6 × 3 m) were laid out in a randomized block design in an existing flat agricultural field, with biochar spread on the surface at rates of either 0 (control), 25 or 50 t ha⁻¹ and incorporated by harrowing. Biochar was derived from mechanically chipped trunks and large branches of *Fraxinus excelsior* L., *Fagus sylvatica* L. and *Quercus robur* L. pyrolysed at 450 °C for 48 h (BioRegional HomeGrown[®]; BioRegional Charcoal Company Ltd, Wallington, Surrey, UK). The biochar chip size distribution was between 2 and 20 mm and had a surface area of 39 ± 4 m⁻² g⁻¹. Further physiochemical details of this biochar and the experimental field trial are provided in Jones *et al.* (2012) and Quilliam *et al.* (2012b). Four replicate soil samples (0 – 20 cm) were taken from each of the 0 and the 50 t ha⁻¹ plots and within 1 h of collection the soil was sieved to pass 5 mm and used for chemical analysis within 24 h.

Speciation of 16 PAHs was determined using Gas Chromatography and Mass Spectrometry (GC-MS), by a commercial accredited laboratory (ALcontrol, Hawarden, UK). Soluble organic compounds were extracted from 5 g of homogenized sample with 20 ml hexane : acetone : triethylamine in the ratio 50 : 45 : 5 (v/v) using the CEM Microwave Accelerated Reaction System. Soil pH and electrical conductivity (EC) were determined on field-moist soil (1 : 1 w/v soil-to-distilled water) with standard electrodes. Biochar surface area was measured by BET multipoint nitrogen adsorption at 77 K (MCA Services, Cambridge, UK). Water content was determined gravimetrically by drying at 105 °C (24 h) and SOM calculated by measuring loss on ignition at 450 °C. Total dissolved C and N were determined in 1 : 5 (w/v) soil : distilled water extracts (Jones & Willett, 2006) with a TCN-V analyzer (Shimadzu Corp., Kyoto, Japan). Available P was determined in 0.5 M acetic acid extracts (1 : 5 w/v) using the colorimetric methods of Murphy & Riley (1962). Measurements of basal soil respiration at quasi-steady state were made on 40 g of field-moist soil for 24 h at 20 °C using an automated multichannel SR1 infrared gas analyser soil respirometer (PP Systems, Hitchin, UK), and substrate-induced respiration quantified following the addition of a solution containing 50 mM glucose, 1 mM KH₂PO₄ and 5 mM KNO₃.

Mineralization of the PAH compound phenanthrene in two agricultural soils

The effect of biochar soil amendments on mineralization was determined in two contrasting agricultural soils, i.e. a Eutric Cambisol (described above) and a Cambic Podzol (collected from the surface Ah horizon (5–20 cm) of an upland (200 m altitude) freely draining, heavily leached, lightly sheep-grazed grassland that receives no fertilization). One of the following four different amendments was combined with 10 g of each soil type in a fully factorial design and replicated in triplicate: (i) control with no amendment; (ii) 0.5 g acid-washed fine quartz sand; (iii) 0.5 g fresh mixed hardwood biochar (BioRegional HomeGrown® - described above); (iv) 0.5 g of a commercial rice husk derived biochar (pyrolysed at 300–600 °C for 0.5–5 h; particle size diameter <2 mm; surface area of $3.74 \pm 0.04 \text{ m}^{-2} \text{ g}^{-1}$; Pyro-6®; Pro Green Charcoal Machines, Pro-Natura, Paris, France).

Phenanthrene labelled with ^{14}C was dissolved in hexane (1000 mg l^{-1}). Each type of biochar, together with an inert control treatment (fine quartz sand) was added to individual 50 ml polypropylene tubes and contaminated with either a high (1.7 mg kg^{-1}) or a low ($0.0017 \text{ mg kg}^{-1}$) concentration of the ^{14}C phenanthrene solution, and transferred to a fume hood for 30 min to allow the hexane to evaporate. The amendments were then thoroughly mixed with 10 g of soil (for the unamended control, the phenanthrene was added directly to the soil and mixed) and a 1 ml alkali trap (1M NaOH in a plastic scintillation vial) added to each tube, sealed with an air tight lid and incubated in the dark at 10 °C (the average annual temperature for these soils). Mineralization of ^{14}C -phenanthrene was assessed over a 166-day incubation period by measuring the release of $^{14}\text{CO}_2$ (captured in the alkali trap). At each time point the NaOH traps were changed and mixed with 5 ml Scintisafe 3® scintillation cocktail (Fisher Scientific, Leicestershire, UK). The amount of $^{14}\text{CO}_2$ captured was quantified using a Wallac 1404 liquid scintillation counter (Wallac EG&G, Milton Keynes, UK).

Leaching of phenanthrene through agricultural soils amended with biochar

To determine the effect of biochar amendment on the subsequent leaching of PAHs the same factorial experimental design as described above was repeated, but to increase the sensitivity two higher ^{14}C phenanthrene contamination levels (0.05 and 5 mg kg^{-1}) were used. Artificial rain water solution ($96 \mu\text{M NaCl}$; $10 \mu\text{M K}_2\text{SO}_4$; $5 \mu\text{M CaCl}_2$; $6 \mu\text{M MgCl}_2$; $15 \mu\text{M NH}_4\text{NO}_3$; $0.1 \mu\text{M KH}_2\text{PO}_4$) was added to each tube and the ^{14}C -phenanthrene in the leachate quantified 24 h later. To allow the collection of leachate the bottom 2 cm of each 50 ml polypropylene tube was cut off and replaced with a 0.2 mm nylon mesh and positioned above collection vials.

Statistical analyses

Differences in soil quality and PAH concentrations in biochar were compared using analysis of variance (ANOVA) and Tukey multiple comparison tests (Minitab 12.0 software, Minitab Inc., State College, PA, USA). A one-way ANOVA was used to compare mineralization of phenanthrene at the final time point and a two-way ANOVA was used to compare differences in leaching of phenanthrene.

Results

Soil and biochar properties

The physio-chemical properties of the Podzol were very different to the Eutric Cambisol (Table 1), with significantly lower pH and EC ($P < 0.05$), and much higher TDN, DOC and organic matter content ($P < 0.01$). However, 3 years after biochar addition, the characteristics of the Cambisol containing wood biochar were not significantly different to unamended soil (Table 1). The rate of basal respiration was no different between the soil types; although substrate-induced respiration was

Table 1 Soil properties of two agricultural soils, and soil amended with wood biochar for 3 years

	Cambic Podzol	Eutric Cambisol	Eutric Cambisol + biochar (50 t ha ⁻¹)
pH	4.9 ± 0.02	6.30 ± 0.01	6.8 ± 0.2
EC ($\mu\text{S cm}^{-1}$)	27 ± 15	98 ± 4	95 ± 3
Moisture content (% of dry weight)	24.2 ± 3.9	15.7 ± 1.4	17.6 ± 0.9
Organic matter (% of dry weight)	12.1 ± 0.3	7.5 ± 0.2	7.6 ± 1.1
Dry bulk density (g cm^{-3})	0.19 ± 0.001	1.04 ± 0.02	1.08 ± 0.07
Total dissolved N (mg N kg^{-1})	22.6 ± 1.6	4.52 ± 0.2	4.62 ± 0.5
Dissolved organic C (mg C kg^{-1})	412 ± 13	16.9 ± 0.8	16.2 ± 0.3
Available P (mg P kg^{-1})	22.0 ± 2.0	10.0 ± 0.36	11.7 ± 2.58
Respiration ($\text{mg CO}_2 \text{ C kg}^{-1} \text{ d}^{-1}$)	0.68 ± 0.23	0.55 ± 0.05	0.71 ± 0.06
*SIR ($\text{mg CO}_2 \text{ C kg}^{-1} \text{ d}^{-1}$)	3.74 ± 1.02	5.72 ± 0.36	6.11 ± 0.28

Values represent the mean of four replicates ± SE.

*SIR, substrate-induced respiration: quantified following the addition of a solution containing 50 mM glucose, 1 mM KH_2PO_4 and 5 mM KNO_3 .

significantly lower ($P < 0.05$) in the Podzol compared to the Eutric Cambisol (with or without biochar addition). The concentration of the USEPA 16 PAHs in the rice husk biochar (64.65 mg kg^{-1}) was significantly higher ($P < 0.001$) than that in the wood biochar (9.56 mg kg^{-1}), with naphthalene being the dominant PAH compound in both biochar types (Table 2). The concentration of total PAHs was significantly higher in the Cambisol compared to the Podzol ($P < 0.05$), and PAH concentration was higher in the Cambisol that had been amended with biochar 3 years previously ($P < 0.05$) compared to the unamended soil.

Mineralization of phenanthrene in two agricultural soils amended with biochar

Mineralization of ^{14}C phenanthrene in both soil types was significantly decreased when amended with biochar ($P < 0.001$) compared to unamended or sand-amended soil (Fig. 1). However, there was no difference in mineralization between the two types of biochar in both the Podzol and the Cambisol contaminated with the low level of phenanthrene, whereas in the Cambisol with the high contamination significantly less mineralization occurred in the soil amended with rice husk biochar than wood biochar ($P < 0.001$). In both soil types, the addition of sand contaminated with the low level of phenanthrene led to significantly higher levels of mineralization compared to the control ($P < 0.001$). In

contrast, mineralization in the biochar-amended Podzols was not significantly affected by the initial level of phenanthrene contamination (Figs 1c and d) and less than 6% ^{14}C phenanthrene was captured as $^{14}\text{CO}_2$. Microbial breakdown of phenanthrene in the Podzol was significantly lower in both the control soil and the soil containing the contaminated sand with the high levels of phenanthrene compared to the other soil types ($P < 0.001$).

Leaching of phenanthrene through biochar-amended soil

In both soil types, at both contamination levels, the amount of leached phenanthrene increased with increasing volume of simulated rainfall ($P < 0.01$; Fig. 2). Although there were no significant differences in the amount of phenanthrene leached in the Eutric Cambisol with the low level of contamination (Fig. 2a), differences in phenanthrene leaching were observed in the three other soils ($P < 0.01$). In the two soils with the high level of phenanthrene contamination (Figs 2b and d), the amount of ^{14}C -phenanthrene leached was significantly lower in the soil containing the rice husk biochar ($P < 0.01$). However, in the Podzol with the low level of contamination (Fig. 2c), the level of leached ^{14}C -phenanthrene was higher in both the biochar treatments ($P < 0.001$). In addition, these two treatments produced the highest level of phenanthrene leachate of any of the soil-treatment combinations ($P < 0.01$).

Table 2 Concentration of polycyclic aromatic hydrocarbons (PAH) in two types of biochar, two types of agricultural soil and soil amended with biochar for 3 years

PAH ($\mu\text{g kg}^{-1}$)	Rice husk biochar	Wood biochar	Cambic Podzol	Eutric Cambisol	Eutric Cambisol + wood biochar (50 t ha^{-1})
Naphthalene	27 100 \pm 1800	6683 \pm 332	39 \pm 5	13 \pm 1	23 \pm 0.7
Acenaphthylene	5265 \pm 265	774 \pm 133	BD	BD	15 \pm 1.3
Acenaphthene	2140 \pm 30	214 \pm 25	BD	BD	BD
Fluorene	6415 \pm 345	237 \pm 11	BD	BD	BD
Phenanthrene	9920 \pm 380	789 \pm 191	44 \pm 13	40 \pm 6	111 \pm 35
Anthracene	3235 \pm 145	144 \pm 34	BD	BD	29 \pm 4
Fluoranthene	3145 \pm 135	269 \pm 61	72 \pm 14	152 \pm 34	291 \pm 34
Pyrene	3720 \pm 180	314 \pm 68	57 \pm 8	142 \pm 35	262 \pm 34
Benz(a)anthracene	1001 \pm 79	40 \pm 9	49 \pm 12	116 \pm 23	169 \pm 17
Chrysene	968 \pm 82	31 \pm 10	49 \pm 14	102 \pm 28	169 \pm 18
Benzo(b)fluoranthene	619 \pm 93	40 \pm 4	89 \pm 26	190 \pm 44	274 \pm 54
Benzo(k)fluoranthene	115 \pm 9	BD	23 \pm 3	68 \pm 20	116 \pm 19
Benzo(a)pyrene	556 \pm 74	23 \pm 4	52 \pm 13	127 \pm 30	198 \pm 22
Indenol(1,2,3-cd)pyrene	160 \pm 28	BD	40 \pm 5	79 \pm 20	121 \pm 12
Dibenzo(a,h)anthracene	64 \pm 9	BD	BD	BD	BD
Benzo(g,h,i)perylene	188 \pm 29	BD	39 \pm 5	94 \pm 23	151 \pm 19
Total PAH (USEPA 16)	64 650 \pm 3650	9556 \pm 722	557 \pm 124	1131 \pm 275	1953 \pm 222

Values represent the mean of four replicates \pm SE. BD, below detection limits.

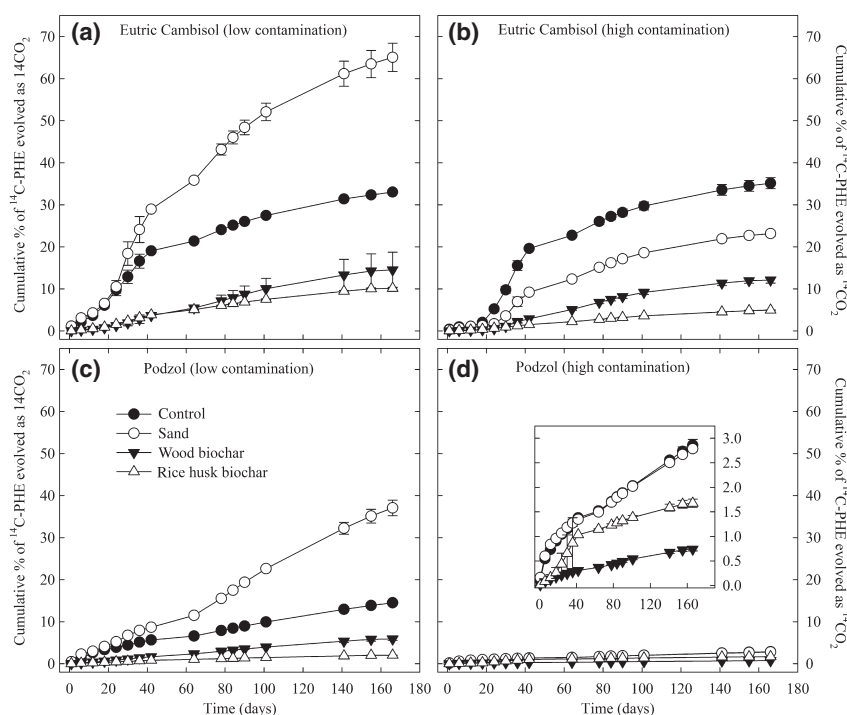


Fig. 1 Mineralization of ^{14}C -phenanthrene (^{14}C -PHE) in two contrasting agricultural soils. Soils were either non-amended (closed circle) or amended with phenanthrene contaminated sand (open circle), wood biochar (closed triangle) or rice husk biochar (open triangle) at either a low (a, c; $0.0017 \text{ mg kg}^{-1}$) or high (b, d; 1.7 mg kg^{-1}) concentration of ^{14}C phenanthrene solution. Insert figure in panel D shows the same data, but on a different scale. Data points represent the mean of four replicates \pm SE.

Discussion

The chemical composition of biochar feedstock will greatly influence the amount and frequency of PAH reactions occurring during pyrolysis. In addition, the temperature and duration of pyrolysis can also make a significant difference to the concentrations of PAHs, e.g. PAHs are more likely to be lost to the atmosphere as gases during a slower and longer pyrolysis residency time, whereas during a fast pyrolysis they are more likely to condense back onto the biochar surface (Hale *et al.*, 2012a). However, despite the concentration of PAHs in the rice husk biochar being nearly seven times greater than that in the wood biochar, the surface area available for PAH adsorption was far lower for the rice husk biochar, and it is likely that the elevated concentrations of PAHs were due to the initial chemical composition of the feedstock (Hale *et al.*, 2012a).

Three years after the addition of wood biochar to a temperate agricultural soil, the PAH concentration was significantly higher than that in unamended soil suggesting that biochar can act as a source of soil contaminants. However, the level of PAHs in the soil remained within the maximum acceptable concentration for a number of European countries, $5\text{--}50 \mu\text{g g}^{-1}$ (Carlson, 2007). The higher levels of PAH compounds in the soil,

however, may have been due to the way the soil was processed, with small fragments ($<5 \text{ mm}$) being analysed as part of the total soil sample. This makes it very difficult to assess whether the soil itself contained the PAH, or whether the increase in concentration was mostly due to quantification of the PAHs that had remained adsorbed to the biochar since its application 3 years previously.

Soils inherently contain complex autochthonous microbial communities, which will have contrasting PAH degrading abilities (Ding *et al.*, 2010). Both soil types used in this study contained detectable concentrations of 11 of the 16 USEPA PAHs, with significantly higher levels in the Eutric Cambisol compared to the Cambic Podzol, the lower pH of which may have been important for influencing the breakdown of PAHs (Kastner *et al.*, 1998). In addition, the Podzol had much higher levels of SOM and dissolved organic C content, which have previously been suggested to lead to higher PAH concentrations due to the higher sorptive capacity of the soil (MacLeod & Semple, 2002). Black C (a collective term for the remnants of incomplete combustion, e.g. soot, fly ash and charcoal) can adsorb PAHs 10–1000 times more strongly per unit mass than other types of organic C in soils (Jonker & Koelmans, 2002; Accardi-Dey & Gschwend, 2003; Rhodes *et al.*, 2010), and

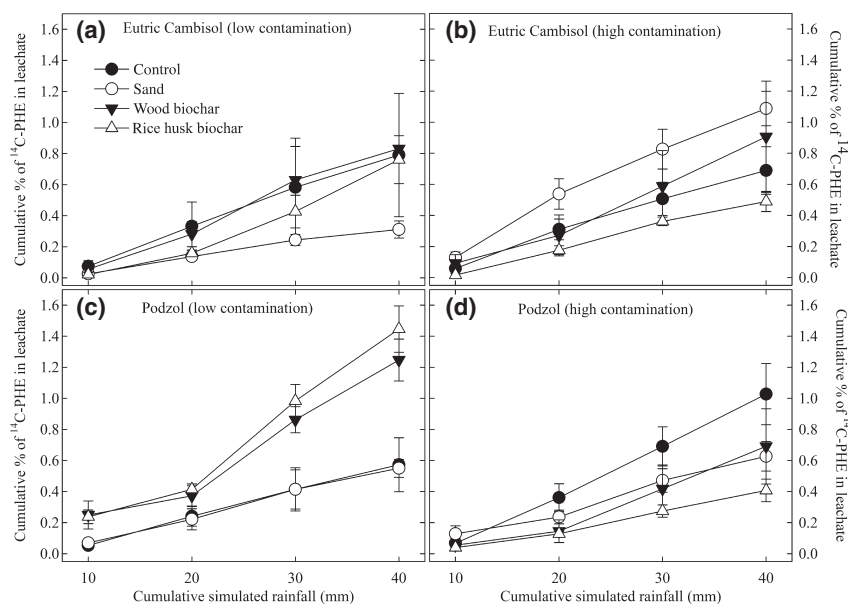


Fig. 2 Leaching of ^{14}C -phenanthrene through two contrasting agricultural soils. Soils were either non-amended (closed circle) or amended with contaminated sand (open circle), wood biochar (closed triangle) or rice husk biochar (open triangle) at either a low (a; c; 0.05 mg kg^{-1}) or a high (b; d; 5 mg kg^{-1}) concentration of ^{14}C phenanthrene solution. Data points represent the mean of four replicates \pm SE.

biochar could thus act as a sink for PAH compounds in soil by strongly adsorbing and physically entrapping them within its pores (Downie *et al.*, 2009). Mineralization of ^{14}C -phenanthrene in the non-amended control Eutric Cambisol agricultural soil, with high and low levels of PAH contamination was at least twice as high as mineralization in the Podzol suggesting that it contained a native soil microbial community more effective at catabolizing PAHs, or simply contained a greater microbial biomass (indicated by the higher rate of substrate-induced respiration). Alternatively, the intrinsic nature of these two contrasting soil types could influence the relevant bioavailability of PAH compounds (e.g. through adsorption to SOM), or by differing concentrations of available minerals, such as P, which could limit potential rates of microbial respiration in the two soils.

Microbial catabolism was clearly influenced by biochar addition to artificially contaminated soils, with lower levels of ^{14}C -phenanthrene mineralization compared to the unamended soil. It is still not clear, however, whether this is driven by the biochar directly influencing biological processes, e.g. abundance and activity of microbial communities, or by physically altering the bioavailability of the PAH by strongly adsorbing it. In both soil types contaminated with the low concentration of ^{14}C -phenanthrene, the highest level of mineralization occurred in the soil amended with sand. This may have been due to increased aeration of the soil facilitating aerobic respiration, although a simi-

lar degree of aeration would also have been expected following the addition of biochar. The total level of PAH degradation, however, may have been significantly underestimated as the concentration of native non-labelled PAHs, which were particularly high on the rice husk biochar, would have significantly increased the pool size of total PAHs. Consequently, assuming that at least some of these were bioavailable, our quantification of ^{14}C -phenanthrene mineralization can only be an indication of the total microbial PAH catabolism. Therefore, although it is likely that the lower ^{14}C -phenanthrene mineralization in biochar-amended soils was mainly due to adsorption and decreased bioavailability, the PAH pool dilution effect may have contributed to a relative decrease in catabolism of this particular labelled PAH.

Mineralization of ^{14}C -phenanthrene was substantially lower than that in previous studies using black carbon as a remediation treatment (Rhodes *et al.*, 2008, 2010). This could be due to the biochar feedstock, including potentially higher concentrations of native PAHs in the biochar, different levels of the initial ^{14}C -phenanthrene contamination, or the cooler incubation temperature (10°C compared to 20°C). In soils with the high level of added phenanthrene contamination, mineralization of ^{14}C -phenanthrene was significantly lower in the Podzol compared to that in the Eutric Cambisol. This may have been caused by differences in the composition of the two respective native microbial communities (e.g. relative toxicity to certain components of the community),

or may have been due to more specific differences in soil properties. Bacteria are generally assumed to be the most important group of soil microorganisms involved in the natural biodegradation of PAHs in soils (Kastner *et al.*, 1998) and as prior exposure to PAHs can allow a degree of microbial adaptation (Rhodes *et al.*, 2010), the higher level of background PAHs in the Eutric Cambisol may have slightly modified the phenanthrene catabolism ability of that microbial community. However, microbial breakdown is also influenced by pH (Kastner *et al.*, 1998), with an inhibition of PAH catabolism by soil microbes occurring at the lower pH characteristic of the Podzol. Furthermore, at a lower pH the bacteria to fungal ratio decreases, and compared to bacteria relatively few fungal species are able to utilize PAHs as their sole C source (Boonchan *et al.*, 2000).

It is unlikely that reduced mineralization following biochar addition is due to a decrease in the concentration of unbound phenanthrene (Rhodes *et al.*, 2008) as following a simulated rain event, the amount of ¹⁴C-phenanthrene leached in the biochar-amended Eutric Cambisol was no different than that in the control soil. This could be due to the biochar already being saturated with PAHs, which would result in a higher level of freely available PAHs for microbial degradation. However, the Podzol containing the low level of ¹⁴C-phenanthrene contamination leached a significantly higher level of ¹⁴C-phenanthrene than the control, although it is not clear whether this is due to sorbent saturation, or a specific change in microbial activity, e.g. a critical concentration of PAH inducing PAH degradation or increasing the abundance of functional gene groups (Ding *et al.*, 2010). One of the aims of this experiment was to determine whether or not biochar-amended soil would be less likely to leach PAHs. Our results suggest that biochar does not decrease PAH leaching, and in particular situations could actually increase the concentration of PAHs leached from soil. The addition of fresh biochar to soil results in the release of significant amounts of DOC, and this, together with dust particles from the biochar could be binding PAHs and thus facilitate their leaching through soils. The sorption and size of these small particles could have important downstream implications, e.g. earthworm ingestion of contaminated DOC or dust particles and subsequent bioaccumulation in food chains, or an increased risk of groundwater contamination. Clearly further work needs to be undertaken to address the dynamic between sorbent saturation, microbial activity and particle size and how this relates to the concentration of PAHs in soil solution.

Long-term impacts of biochar additions to soils are still not fully understood, although evidence suggests

that the type of feedstock and the conditions of its manufacture are of central importance. We have shown that biochar can reduce the degradation of PAHs in two important types of agricultural soil, which in the short term could not only increase the concentration of soil PAH but could also affect the long-term persistence of PAHs in the environment. Biochar amendment did not consistently decrease PAH leaching from these two agricultural soils, and despite its strong sorbing capacity, biochar may not be a useful tool for limiting groundwater contamination. Inhibition of PAH mineralization by biochar amendment is probably a consequence of increased sorption and subsequent reduced bioavailability to soil microbial communities. As sorption is a key process in determining the environmental fate of PAHs in soil, improving our understanding of the role biochar plays in sorbing PAHs in a number of different scenarios will provide valuable information for the assessment of biochar risks. Before large scale biochar addition to soils is adopted, future work is needed to address the dynamic between sorbent saturation and microbial activity and how this relates to the concentration of PAHs in soil solution and their persistence in the environment.

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