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Impact of two contrasting biochars on the bioaccessibility of ^{14}C-naphthalene in soil

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HIGHLIGHTS

- Biochar made from differing feedstock and production condition exhibit obvious contrasting properties.
- Biochar exhibiting higher micropore distribution strongly inhibited losses of naphthalene in soils following increase in contact time.
- Indigenous microorganisms expressed the capacity to readily mineralise naphthalene, but as the concentration of biochar increased, the extent of mineralisation decreased due to surface area and microporosity.
- HPCD solution was shown to be a rapid tool to predict bioaccessibility of naphthalene.
- Biochar showed to be a cheap tool to mitigate risk of exposure to PAHs.

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ABSTRACT

This study investigated the impact of two different wood biochars (BioC1 and BioC2) on the extractability and biodegradation of ^{14}C-naphthalene in soil. Both biochars had contrasting properties due to difference in feedstocks and pyrolytic conditions (450–500 °C and 900–1000 °C, designated as BioC1 and BioC2, respectively). This study investigated effects of biochar on the relationship between ^{14}C-naphthalene mineralisation and calcium chloride ($CaCl_2$), hydroxypropyl- β-cyclodextrin (HPCD) or methanol extraction in soil amended with 0%, 0.1%, 0.5% and 1% BioC1 and BioC2 after 1, 18, 36 and 72 d contact times. Total extents of ^{14}C-naphthalene mineralisation and extraction were reduced with increasing concentrations of biochar; however, BioC2 showed greater sorptive capacity. Good linear correlation existed between total extents of ^{14}C-naphthalene mineralisation and HPCD extractions in BioC1 (slope = 0.86, r^2 = 0.92) and BioC2 (slope = 0.86, r^2 = 0.94) amended soils. However $CaCl_2$ and methanol extractions underestimated and overestimated extents of mineralisation, respectively. These results indicate that biochar can reduce the bioaccessibility of PAHs and the corresponding risk of exposure to biota, whilst HPCD extraction estimated the bioaccessible fraction of PAHs in soil. Bioaccessibility assessment is vital in evaluation of biodegradation potential and suitability of bioremediation as a remediation option.

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1. Introduction

Black carbon (BC) encompasses naturally occurring soot and char in the environment as well as some other by-products of natural and anthropogenic activities (Koelmans et al., 2006; Rhodes et al., 2008a). Previous studies have investigated the ability of biochar to sequester atmospheric CO_2 in soil to aid climate change mitigation (Schmidt and Noack, 2000; Lehmann and Rondon, 2006). Additionally, biochar has been shown to increase soil nutrients to encourage plant growth (Glaser et al., 2002), improve soil characteristics (Asai et al., 2009) and stimulate other biological functions (Lehmann et al., 2006). Furthermore, biochar has an intrinsic ability to effectively sequester organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins, and bisphenol A (Chen and Yuan, 2011; Hale et al., 2011; Sun et al., 2011; Chai et al., 2012; Ogbonnaya and Semple, 2013). The organic contaminant sorption characteristics of biochar have been attributed to large surface area (Thies and Rillig, 2009) and high porosity (Özçimen and Ersoy-Meriçboyu, 2010), which results in decreased mobility and bioaccessibility of the contaminants (Beesley et al., 2010; Marchal et al., 2013). Some factors exist which affect biochar properties and consequently the capacity to influence the contaminant bioavailability in soils. These factors include (a) the source biomass (feedstock) and (b) the production method (pyrolysis) (Ogbonnaya and Semple, 2013; Verheijen et al., 2010). Therefore, the biomass feedstock for the pyrolysis process is important in determining the resulting biochar properties. Varying biochar characteristics occur as feedstock biomass materials differ; wood chip, tree bark and crop residues, others can be sourced from poultry litter, dairy manure and sewage sludge (Das et al., 2008; Sohi et al., 2009).

Contaminated land practitioners also require reliable and robust techniques to determine the applicability of biodegradation and reduce the exposure of contaminants to receptors. Hydroxypropyl-β-cyclodextrin (HPCD) extraction has been shown to predict extents of microbial mineralisation of spiked PAHs at varying concentrations, time and in different soils (Reid et al., 2000; Patterson et al., 2004; Allan et al., 2006; Doick et al., 2006; Rhodes et al., 2008b; Ogbonnaya et al., 2014). Semple et al. (2007) referred the endpoint of biodegradation as the bioaccessible fraction. HPCD extraction has further been effective in predicting biodegradation of co-contaminated soils (Doick et al., 2005; Stroud et al., 2009), field contaminated soils (Stokes et al., 2005a; Papadopoulos et al., 2007) and sediments (Cuypers et al., 2002). HPCD extraction clearly represents the fraction of PAHs loosely partitioned to soil matrix and fraction of PAH in the aqueous phase available for biodegradation (Paton et al., 2009).

Moreover, Rhodes et al. (2008a) investigated the potential of HPCD extractability to predict ^{14}C-phenanthrene mineralisation in activated carbon (AC) amended soils. The authors showed that HPCD extraction underestimated extent of ^{14}C-phenanthrene mineralisation in >0.1% AC amended soils. In addition, Rhodes and collaborators suggested that such concentrations of AC in soils affect bioaccessibility of PAHs and would affect regulatory procedures. Consequently, the presence of such BC substances can influence the exposure of contaminants to receptors. Therefore the aim of this study was to test investigate (i) the effect of two contrasting wood biochars on the mineralisation of ^{14}C-naphthalene by indigenous microflora; (ii) the extractability of ^{14}C-naphthalene using calcium chloride ($CaCl_2$), HPCD and methanol solutions; (iii) the correlation between amounts of ^{14}C-naphthalene mineralised to ^{14}C-naphthalene extracted; (iv) the correlation between maximum rate of ^{14}C-naphthalene mineralisation to amount of ^{14}C-naphthalene extracted.

2. Materials and methods

2.1. Chemicals

Non-labelled (^{12}C) naphthalene was obtained from BDH laboratory supplies, UK and [9-^{14}C] naphthalene (>95% radioactive purity) was obtained from Sigma Aldrich Co., Ltd, UK. Goldstar multipurpose liquid scintillation fluid was obtained from Meridian, UK. Hydroxypropyl-β-cyclodextrin (HPCD) was obtained from Fischer Scientific, UK. Calcium chloride (≥99.0%) was obtained from Sigma Aldrich Co., Ltd, UK. Methanol was obtained from Fisher scientific, UK. Sample oxidiser cocktails (Carbotrap and Carbocount) were from Meridian, UK, and Combustaid from Perkin Elmer, USA.

2.2. Soil preparation

An uncontaminated soil (Myerscough soil) classified as surface texture of sandy loam was used in this study. The physicochemical characteristics of the soil can be found in Table 1. The soil was air-dried for 24 h and passed through a 2 mm sieve to remove stones and plant roots. The moisture content of the soil was determined by drying 2 g samples of the soil ($n = 3$) in porcelain crucibles at 105 °C for 24 h. After drying, the samples were then cooled in a desiccator (1 h) and weighed again.

2.3. Biochars

The first biochar (BioC1) was obtained from Yorkshire Charcoal Co., UK and the second biochar (BioC2) was obtained from O-Gen UK. Plate count agar and agar-agar were supplied by Oxoid, UK. BioC1 was produced by slow pyrolysis (16–18 h duration at 450–500 °C) of a feedstock containing approximately 90% *Acer*, and the remaining 10% a mixture of *Quercus* and