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Opening the black box: Soil microcosm experiments reveal soot black carbon short-term oxidation and influence on soil organic carbon mineralisation



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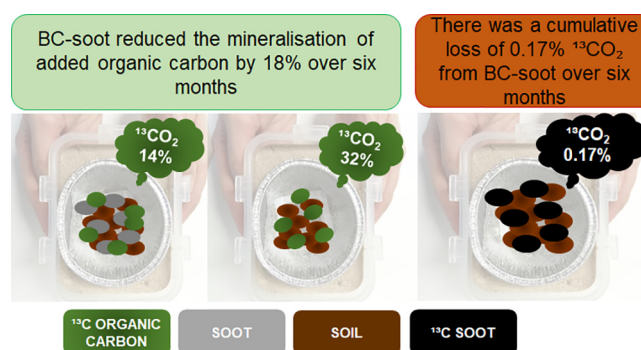
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HIGHLIGHTS

- Black carbon (BC) influence on soil organic carbon mineralisation was studied.
- The stability of BC in soil over short timescales was investigated.
- BC-soot reduced the mineralisation of added organic carbon by 18%.
- BC-biochar did not influence the mineralisation of added organic carbon.
- There was a cumulative loss of 0.17% ¹³C from BC-soot over six months.

GRAPHICAL ABSTRACT



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ABSTRACT

Soils hold three quarters of the total organic carbon (OC) stock in terrestrial ecosystems and yet we fundamentally lack detailed mechanistic understanding of the turnover of major soil OC pools. Black carbon (BC), the product of the incomplete combustion of fossil fuels and biomass, is ubiquitous in soils globally. Although BC is a major soil carbon pool, its effects on the global carbon cycle have not yet been resolved. Soil BC represents a large stable carbon pool turning over on geological timescales, but research suggests it can alter soil biogeochemical cycling including that of soil OC. Here, we established two soil microcosm experiments: experiment one added ¹³C OC to soil with and without added BC (soot or biochar) to investigate whether it suppresses OC mineralisation; experiment two added ¹³C BC (soot) to soil to establish whether it is mineralised in soil over a short timescale. Gases were sampled over six-months and analysed using isotope ratio mass spectrometry. In experiment one we found that the efflux of ¹³C OC from soil decreased over time, but the addition of soot to soil significantly reduced the mineralisation of OC from 32% of the total supplied without soot to 14% of the total supplied with soot. In contrast, there was not a significant difference after the addition of biochar in the flux of ¹³C from the OC added to the soil. In experiment two, we found that the efflux ¹³C from soil with added ¹³C soot significantly differed from the control, but this efflux declined over time. There was a cumulative loss of 0.17% ¹³C from soot over the experiment.

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These experimental results represent a step-change in understanding the influence of BC continuum on carbon dynamics, which has major consequences for the way we monitor and manage soils for carbon sequestration in future.

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1. Introduction

There is approximately three times more carbon found in soils than is held in the atmosphere as CO₂ (Fischlin et al., 2007; Lal, 2004; IPCC, 2019). However, global shifts in land-use from natural and semi-natural ecosystems to agricultural and urban land, along with agricultural intensification have heavily degraded soils, with the resultant loss of an estimated 40 to 90 Pg of soil organic carbon (SOC) (Smith, 2007). As a direct response, signatories of the Kyoto Protocol are required to quantify the amount of carbon stored in soils, in order to monitor the net carbon emissions to the atmosphere by changes in land management or land-use. In spite of the critical role soils play in the global carbon cycle, we fundamentally lack detailed mechanistic understanding of the turnover of major soil organic carbon pools, particularly so-called black carbon (BC). This limits our ability to integrate soils into policies for a net zero future.

Black carbon is the product of the incomplete combustion of biomass and fossil fuels (Masiello, 2004; Hedges et al., 2000; Kuhlbusch and Crutzen, 1995). As such, the term BC describes a continuum of particles from slightly charred biomass to highly condensed and refractory soot and graphite (Bird et al., 2015; Hedges et al., 2000; Kuhlbusch and Crutzen, 1995). Slightly charred particles are generally dominated by small polycyclic aromatic hydrocarbons (PAHs) (2-7 rings) and labile carbon forms and, whereas soot particles are mainly comprised of gas phase re-condensed highly aromatic molecules (PAHs >7 rings) and stable carbon forms (Bird et al., 2015; Koelmans et al., 2006; Meredith et al., 2012). Black carbon occurs ubiquitously in the environment, playing an important role in a wide range of biogeochemical processes (Talukdar et al., 2019; Bond et al., 2013; Flanner, 2013; Masiello, 2004), and it has been suggested that it may influence the turnover of more labile ecosystem-derived SOC, defined as decaying plant residues, soil biota and exudates (Liu et al., 2018; Edmondson et al., 2015; Liang et al., 2010; Major et al., 2010). Overall, it is estimated that global BC soil stocks range between 54 and 109 Pg, representing the largest pool in the BC cycle (Bird et al., 2015). BC has been demonstrated to contribute to a significant portion of the total organic carbon (TOC) pool; e.g. in urban soils >20% (Edmondson et al., 2015; Hamilton and Hartnett, 2013; Liu et al., 2011; Rawlins et al., 2008) and in agricultural soils between 2 and 42% (Lavalée et al., 2019; Hamilton and Hartnett, 2013; Skjemstad et al., 2002). However, the methods used to determine soil carbon stocks do not consistently quantify BC, with the current state-of-the-art deploying CN elemental analysis which does not distinguish between ecosystem-derived carbon and BC (Edmondson et al., 2015). In contrast, alternative approaches such as dichromate oxidation mostly target the more labile ecosystem-derived carbon (Reisser et al., 2016; Knicker et al., 2007). As a direct result, the differential outputs of current analytical methodologies render national carbon inventories incomparable. For example, across Continental Europe and Northern Ireland BC is quantified as part of the TOC pool via elemental analysis (de Brogniez et al., 2015; Xu et al., 2011), while BC is not accounted for in England, Wales (Bradley et al., 2006) and the Republic of Ireland (Cruickshank et al., 1998) where soil carbon measure are derived from dichromate oxidation.

Although BC is ubiquitous in soils globally, our understanding of its contribution to the SOC cycle and the biogeochemical global carbon cycle is poorly resolved (Smith et al., 2015). Understanding of the influence of BC on the SOC cycling and its stability in soils is crucial for climate change mitigation policies due to its potential to offset carbon emission and increase carbon sequestration and to increase the

accuracy of global carbon models simulating carbon cycling under different climate change scenarios (Cotrufo et al., 2016).

Research on the influence of BC on the turnover of more labile, ecosystem-derived SOC, include both suppression and stimulation of SOC mineralisation (Whitman et al., 2015). Liu et al. (2018) reported that addition of biochar (a form of BC) to the soil decreased the cumulative emission of CO₂ between 72% to 88% compared to control without biochar. Similarly, Liang et al. (2010) observed that total carbon mineralisation in BC-rich soils was 25.5% lower than in BC-poor adjacent soils. In contrast, Major et al. (2010) observed that 41% and 18% more carbon was respired when biochar was added to the soil compared to control, in two consecutive years. BC represents a largely stable pool of carbon turning over on geological timescales (Lehmann, 2015; Singh et al., 2012; Preston and Schmidt, 2006; Masiello, 2004; Goldberg, 1985). However, studies have reported soil BC mineralisation at shorter timescales (Major et al., 2010; Cheng et al., 2006; Hamer et al., 2004), although most of this work is carried out in the context of the more labile biochar, as opposed to soot, which is the more recalcitrant component of the BC continuum, but is a major feature of soils in the industrialised world (Hamilton and Hartnett, 2013; Liu et al., 2011; Sánchez-García et al., 2012; Stanmore et al., 2001). To date, no studies have investigated the stability of soot in soils and its role in the mineralisation of ecosystem-derived organic carbon. To provide a fundamental advance in our understanding of the extent to which BC represents an active component in the soil carbon cycle, we established two microcosm experiments in combination with isotope tracer technology and gas analysis to address two fundamental questions: a) Does BC (soot and biochar) influence the mineralisation of ecosystem-derived carbon pools? and b) Is BC in the form of soot mineralised in soils over short time scale?

2. Material and methods

2.1. Experimental microcosm soil

Soil for the microcosm experiment was sampled, in triplicate, from an arable farm in Lincolnshire, UK (53°18' 52.1" N, 0° 26' 17.6" W), in February 2019. The soil samples were subsequently mixed, air-dried and passed through a 2 mm sieve. Prior to analyses, a subsample of this soil was homogenised in an agate ball-mill and sieved to 2 mm to remove any stones. Soil texture was determined by Laser Scattering Particle Size Distribution Analyser (Horiba LA 950): prior analyses, TOC was removed by addition of H₂O₂ (9.8 M) to 10 g of soil (Mikutta et al., 2005). Soil pH was measured in a 1:2.5 soil to water solution. Soil TOC concentration was determined in a CN analyser (Vario EL Cube, Elementar, Hanau, Germany) (Edmondson et al., 2012). Before TOC analyses, inorganic carbon was removed by addition of 700 µl of HCl (6 M) to 90 mg of soil (Rawlins et al., 2008). Soil BC concentration was analysed by hydroxyprolyses (HyPy), described in detail elsewhere (Meredith et al., 2012). The microcosm soil had a pH of 6.73 and a sandy loamy texture. Soil TOC was 28.72 ± 0.84 mg g⁻¹, of which more than 95% was ecosystem-derived organic carbon (26.64 ± 0.91 mg g⁻¹), with a BC concentration of 2.08 ± 0.09 mg g⁻¹.

2.2. Soot and biochar production and characterization

Samples of soot particulate matter (PM) were generated from methane gas under pyrolysis conditions in an electrically heated flow tube reactor. The equipment and method of particulate generation has been

described previously (Eveleigh et al., 2014), and adaptations have been made to the equipment to collect soot PM onto filter papers (Dandajeh et al., 2017). Separate soot PM samples were collected from methane of natural isotopic composition (BOC, UK), and isotopically labelled ^{13}C methane (99% ^{13}C , Sigma Aldrich). The reactor temperature was controlled to 1200 °C gas temperature at the reactor centreline. Flow rates of 20 l min $^{-1}$ nitrogen and 207 ml min $^{-1}$ of methane were metered by mass flow controllers, resulting in 10,000 ppmv methane concentration. The flow rates resulted in a residence time through the reactor zone of constant heating of ~1 s. Particulate matter was sampled from the reactor centreline and drawn through a stainless-steel sampling tube under vacuum and filtered through glass fibre filters (70 mm filter, 0.7 μm pore size) onto which soot PM was deposited. A total mass of about 0.55 g particulate was collected onto several filters (a total of about 100 mg per filter), for both natural and isotopically labelled methane.

Biochar samples were produced from willow chips using a laboratory pyrolysis unit at the UK Biochar Research Centre at the University of Edinburgh. Approximately 30 g of willow chips were placed in a laboratory batch pyrolysis unit with a vertical quartz tube (inner diameter 50 mm) externally heated by a 12 kW infra-red gold image furnace (P610C; ULVAC RIKO, Yokohama, Japan) described in detail elsewhere (Mašek et al., 2018; Crombie et al., 2013). Before pyrolysis, the reactor was purged with nitrogen to eliminate any residual air within the system. The nitrogen purge was maintained at a rate of 0.3 l min $^{-1}$ for the duration of the experiment. The willow chips were pyrolyzed at a heating rate of 20 °C min $^{-1}$, with the highest treatment temperature (HTT) of 450 °C, and a residence time of 30 min at HTT. After pyrolysis, the system was cooled down under nitrogen flow to prevent oxidation of the biochar.

Soot and biochar samples were analysed using HyPy (Meredith et al., 2012). HyPy tests were performed using the procedure described previously by Ascough et al. (2009). The soot and biochar samples were first loaded with 10% by weight of molybdenum (Mo) catalyst using an aqueous/methanol solution of ammonium dioxodithiomolybdate $[(\text{NH}_4)_2\text{MoO}_2\text{S}_2]$ and placed within borosilicate sample holders to allow for the accurate weight loss during pyrolysis of each sample to be determined (Haig et al., 2020). The samples were pyrolyzed with resistive heating from 50 °C to 250 °C at 300 °C min $^{-1}$, and then from 250

°C to 550 °C at 8 °C min $^{-1}$, before being held at the final temperature for 2 min, under a hydrogen pressure of 15 MPa. A hydrogen sweep gas flow of 5 l min $^{-1}$, measured at ambient temperature and pressure, ensured that the products were quickly removed from the reactor, and subsequently trapped on dry ice cooled silica (Meredith et al., 2004).

The dichloromethane soluble products desorbed from the silica were then analysed on an Agilent GC-MS (7890B GC; 5977A MSD), scanning in the mass range of m/z 40-400 (EI 70 eV, source temperature 200 °C). Product separation was performed on an HP-5MS column (30 m \times 250 μm \times 0.25 μm). The GC oven temperature was initially held at 50 °C for 0.5 min, then heated to 300 °C at a rate of 4 °C min $^{-1}$, where it was held for 5 min. Individual compounds were identified using a NIST MS library and published data.

The soot appeared to be very similar in composition to the n-hexane soot described in the BC ring trial (Hammes et al., 2007), with a carbon content 93% (compared with 92.9%), and an atomic H/C of 0.21 (compared with 0.19). As expected, the soot was very stable under HyPy conditions ($\text{BC}_{\text{HyPy}} = 69\%$), although as with the ring trial soot there was a small but significant labile fraction. The biochar carbon concentration was 73% and an atomic H/C of 0.61, similar to atomic H/C of biochars produced at equal pyrolysis temperature (Xiao et al., 2016). Compared to soot, biochar was less stable under HyPy condition ($\text{BC}_{\text{HyPy}} = 52\%$), however within the range of BC_{HyPy} reported in Meredith et al. (2017) for biochars produced at similar temperature.

GC-MS of this labile non- BC_{HyPy} fraction of the soot was dominated by 4-6 ring parent PAHs structures (Fig. 1). This is probably a reflection of the relatively high temperature of formation of the soot, which is known to increase the degree of condensation, and so result in a more restricted distribution of PAHs that are able to be cleaved off by HyPy (Mcbeath et al., 2015; Meredith et al., 2017). For this soot, the formation temperature of 1200 °C has appeared to suppress 2-4 ring PAHs in preference to 5-6 rings, in addition to the much larger clusters that form the stable BC_{HyPy} fraction.

GC-MS of the labile non- BC_{HyPy} fraction of the biochar show it to be very similar to the soot one, dominated by 4-6 rings PAHs structures (Fig. 2), however soot also presented 7 rings PAHs structures (e.g. Coronene, Fig. 1). The labile biochar fraction contained more alkyl-substituted PAHs resulting in multiple clusters of peaks and an

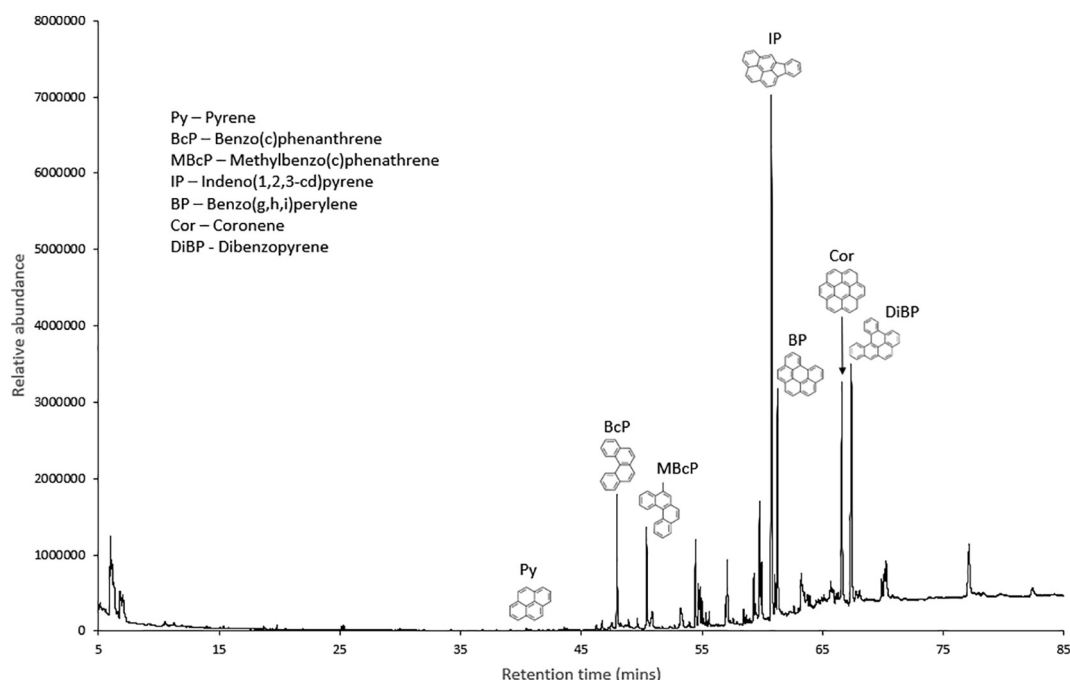


Fig. 1. Total ion chromatogram of the labile non- BC_{HyPy} of the soot.

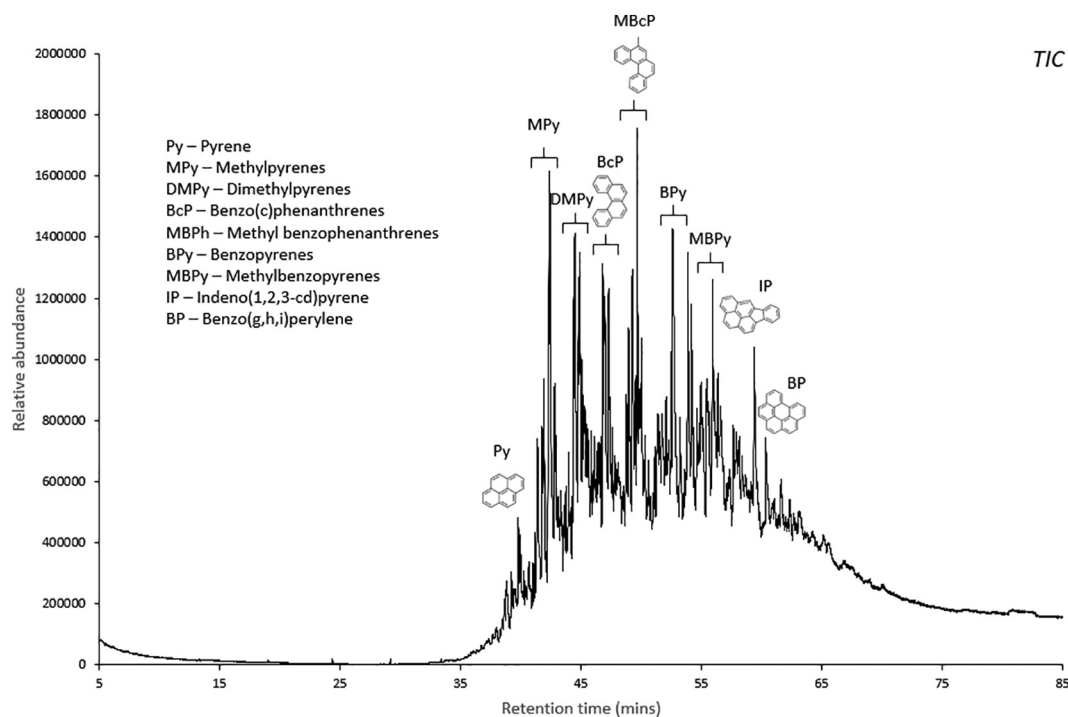


Fig. 2. Total ion chromatogram of labile non-BC_{HyPy} of the biochar.

unresolved complex mixture beneath the baseline (Fig. 2). Biochars and charcoals, especially those formed at relatively low temperatures are typically dominated by 2-4 ring structures (Rombolà et al., 2016; Ascough et al., 2010). In this biochar, the 4 rings structures are the most abundant and the 2-3 rings compounds seems to be suppressed at 450 °C.

2.3. Microcosm experiments

Two microcosm chamber experiments were conducted over 168 days: experiment one added ¹³C labelled organic carbon to soil with and without added BC (soot or biochar) to investigate the influence of soot and biochar on organic carbon mineralisation; experiment two added ¹³C soot to soil to investigate the mineralisation rate of soot in soil.

Experiment one treatments were: control (organic carbon) (soil with 19.42 mg ¹³C organic carbon - 99% ¹³C Sucrose, Sigma Aldrich catalogue number 605417); organic carbon and soot (soil with 19.42 mg ¹³C organic carbon and 25 mg of unlabelled soot) and organic carbon and biochar (soil with 19.42 mg ¹³C organic carbon and 25 mg of unlabelled biochar). Soot and biochar were added into the soil at rate of 10 t ha⁻¹ which represents a common rate of application in soil-BC research experiments (O'Connor et al., 2018; Jeffery et al., 2011). Sucrose, glucose and fructose are often identified as the most abundant low molecular weight carbon compounds present in root exudates, across all ecosystems (Girkin et al., 2018; Shi et al., 2011). Thus, sucrose was selected for this experiment as a common photosynthetically derived form of labile organic carbon found in soils across all ecosystems (Canarini et al., 2019; Girkin et al., 2018; Shi et al., 2011). Sucrose was added at the rate of 3.88 mg C g⁻¹ dry soil which falls between low and medium root exudates input rates previously reported in literature (Basiliko et al., 2012; Girkin et al., 2018; Shi et al., 2011). Experiment two treatments were: control (soil) and soot (soil with 25 mg of ¹³C soot). All treatments were thoroughly mixed into 5 g dry weight equivalent of soil to homogenise and replicated four times. Each treatment was set up in a 180 ml air-tight plastic container and kept in a controlled environment at constant temperature of 18 °C for the duration of the experiment. Ultra-pure water was added to each experimental unit

throughout the duration of the experiment to maintain soil moisture at field capacity. Experiment one ran for 168 days and experiment two ran for 154 days, with measurements at set up and after 1, 7, 14, 21, 28, 35, 42, 49, 56, 70, 84, 98, 112, 126, 140, 154 and 168 days. ¹³CO₂ gases were sampled through a one-way stopcock valve with a 10 ml syringe. To avoid anoxic condition, each experimental unit was opened to oxygenate at each sampling point. Gas samples were analysed for ¹³C content by continuous flow isotope ratio mass spectrometry (SERCON ANCA GSL 20-20 IRMS). According to convention, ¹³C enrichment was expressed as δ¹³C (relative to the Pee Dee Belemnite international standard) using Eq. (1) (Boström et al., 2007).

$$\delta^{13}\text{C} (\text{‰}) = \left(\frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{Sample}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{Standard}}} \right) \times 1000 \quad (1)$$

The cumulative percentage of the CO₂ respired from ¹³C-labelled soot or organic carbon was calculated by pool dilution using Eq. (2).

$$C_l = \sum_{n=n^{\text{th}}}^t \left[\left(\frac{A_r - A_a}{A_s} \right) \times 100 \right] \quad (2)$$

where C_l = Cumulative percent CO₂ lost; t = sampling time point; n = n^{th} sampling time point; A_r = atom% of the ¹³C-CO₂ respired (see Table S2 and S4); A_a = atom% of ¹³C-CO₂ (natural abundance; A_a = 1.09 atom%); A_s = ¹³C atom% of the labelled soot or organic carbon added to the soil.

2.4. Statistical analyses

Linear mixed-effect models were used to analyse the differences between δ¹³CO₂ fluxes in the incubation experiment with or without ¹³C soot and to test for an effect of soot and biochar on ¹³C organic carbon mineralisation over time. The mixed-effect model was applied using the package 'nlme' (Zuur et al., 2009) in R v.3.6.1 (R Core Team, 2017), where the random effect variable was replicate, the fixed effect

variables were treatments and duration of the experiment (Days) and method of estimation Maximum Likelihood (ML). The Akaike information criterion (AIC) was used to compare the performance of different models and identify the best fitting model. To improve normality, $\delta^{13}\text{C}$ modelled data of experiment one were log-transformed prior to statistical analyses. Data below IRMS limit of detection were treated as missing values and thus exclude from the analyses.

3. Results

3.1. Effect of soot and biochar on the mineralisation of added organic carbon

The addition of soot significantly decreased the flux of $\delta^{13}\text{C}$ from the organic carbon added to the soil ($F = 30.152$; d.f. = 1,89; $p < 0.0001$; Fig. 3a). Although the flux of $\delta^{13}\text{C}$ from the organic carbon decreased significantly over time there was a significant interaction between experimental duration (Days) and treatment. The difference between the organic carbon and organic carbon with soot increased over time ($F = 67.372$; d.f. = 2,89; $p < 0.0001$; Fig. 3a). The significant reduction in the flux $\delta^{13}\text{C}$ from organic carbon with soot addition resulted in a reduction in cumulative loss of carbon supplied over the duration of the experiment from 32% without soot to 14% with soot (Fig. 3b). In contrast, there was not a significant difference after the addition of biochar in the flux of $\delta^{13}\text{C}$ from the organic carbon added to the soil ($F = 2.402$; d.f. = 1,92; $p = 0.1246$; Fig. 3c). However, there was a significant interaction between experimental duration (Days) and treatment. The difference between the organic carbon and

organic carbon with biochar slightly increased over time ($F = 23.921$; d.f. = 2,92; $p < 0.0001$; Fig. 3c).

3.2. Mineralisation of soot in soil

The addition of ^{13}C soot significantly increased the flux of $\delta^{13}\text{C}$ when compared to the control ($F = 234.7715$; d.f. = 1,98; $p < 0.0001$; Fig. 4a), however the $\delta^{13}\text{C}$ flux ^{13}C soot added decreased significantly over the duration of the experiment ($F = 5.9169$; d.f. = 2,98; $p = 0.0037$; Fig. 4a). After 24 h 0.0037 mg of the added ^{13}C soot had been mineralised and the cumulative total of mineralised soot increased to 0.039 mg after 168 days (Fig. 4b). The cumulative loss of carbon added as soot over the duration of the experiment was 0.17% (Fig. 4b).

4. Discussion

It is estimated that the global BC soil pool ranges between 54 and 109 Pg, this is the largest pool in the global BC cycle (Bird et al., 2015) with the soot fraction of this BC pool considered to be the most recalcitrant (Masiello, 2004; Hedges et al., 2000; Kuhlbusch and Crutzen, 1995). Here we show, for the first time, that BC in the form of soot suppresses the mineralisation of labile organic carbon in soils, with 18% less ^{13}C produced when soot is added to the soil. In addition, we show that BC in the form of soot can be, to some extent, mineralised in soils and contribute to soil CO_2 effluxes. Together, these findings cast doubt on the widely held assumption that BC in the form of soot plays a passive role in soil carbon dynamics. Black carbon represents an important component of the carbon cycle that is not accounted for

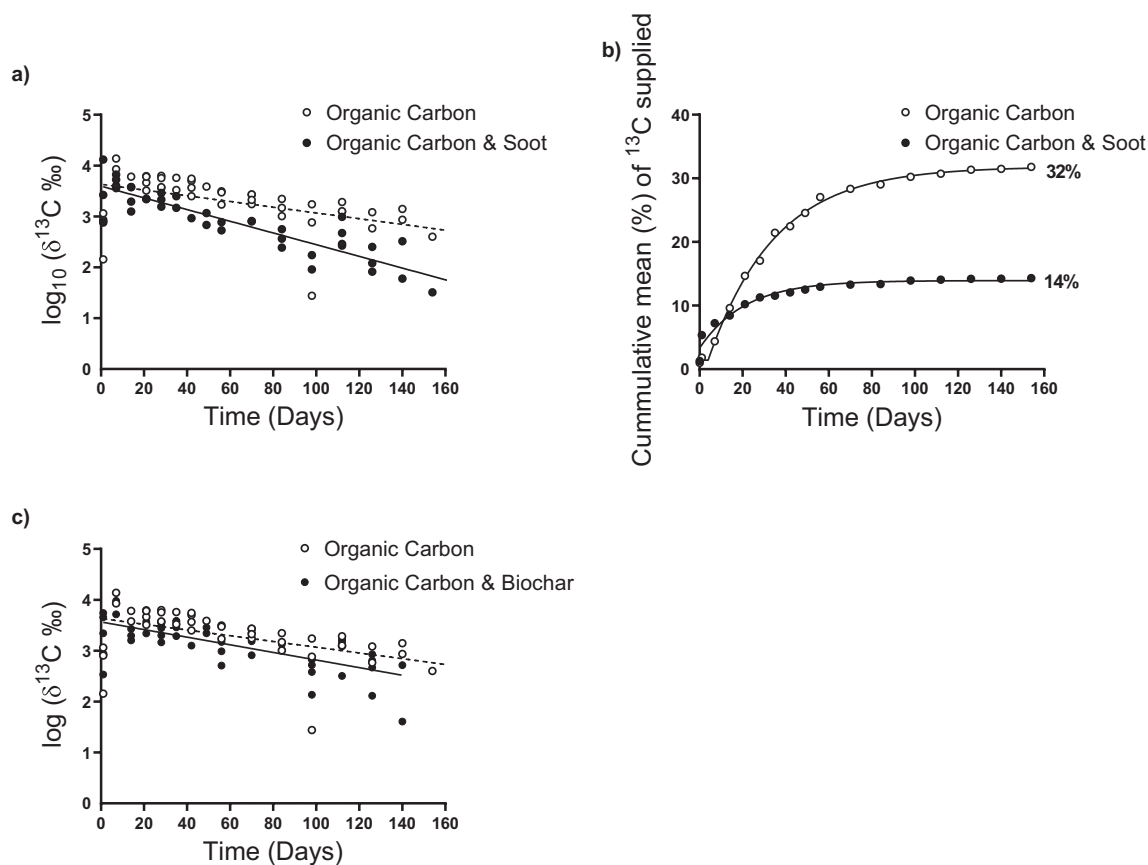


Fig. 3. The effect of the addition of soot and biochar to soil on the evolution of CO_2 from ^{13}C labelled organic carbon over time, a) $\log_{10} \delta^{13}\text{C}$ evolution from soil with added ^{13}C labelled organic carbon and ^{13}C labelled organic carbon and soot, b) mean cumulative loss of ^{13}C supplied as sucrose; standard error bars are too small (see Supporting Information Table S2 for standard error values), c) $\log_{10} \delta^{13}\text{C}$ evolution from soil with added ^{13}C labelled organic carbon and ^{13}C labelled organic carbon and biochar and. Open circles represent soil with ^{13}C organic carbon and closed circles represent soil with ^{13}C organic carbon and BC added.

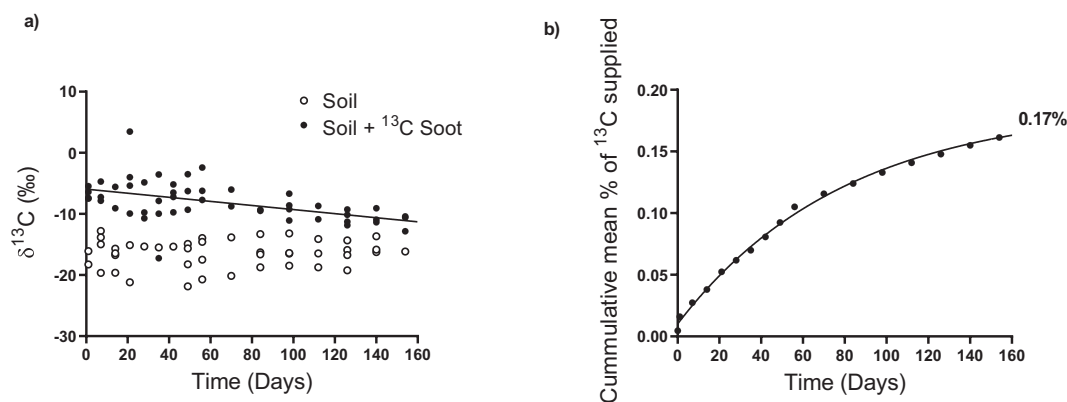


Fig. 4. a) The $\delta^{13}\text{C}$ flux from soil with added ^{13}C labelled soot (closed circles) compared to control soil (open circles), and b) mean cumulative loss of ^{13}C soot supplied from soil for the duration of the experiment; the standard error bars are too small (see Supporting Information Table S4 for standard error values).

in current models of dynamic carbon fluxes between soils and the atmosphere (Cotrufo et al., 2016). This finding is thus fundamental to our understanding of the soil carbon cycle.

While the mechanisms underpinning the suppressive effect of soot on the mineralisation of labile organic carbon need further investigation, the high surface area of soot and the high abundance of surface binding sites (surface groups) increase the reactivity and capability of soot to interact with labile organic carbon (Lehmann, 2015), thus potentially explaining this result. Indeed, it has been demonstrated that BC presents a high sorption affinity for organic carbon compounds (Kasozi et al., 2010), making them less accessible for soil microbes. In particular, adsorption and encapsulation have been suggested as potential mechanisms by which BC may suppress the mineralisation of labile organic carbon (Liu et al., 2018; Whitman et al., 2015; Lu et al., 2014; Zimmerman et al., 2011). In the first mechanism, encapsulation, the organic carbon is adsorbed within the pore of black carbon which became physically unavailable for microbes degradation. In the second mechanism, adsorption, the organic carbon is adsorbed on the large surface area of the black carbon which became less accessible to soil microbes. This result corroborates the previously observed correlation between ecosystem-derived soil organic carbon and soil BC concentration, which in the urban context of this study, was most likely soot (Edmondson et al., 2015; Hamilton and Hartnett, 2013; Liu et al., 2011). Additionally, our findings are supported by research demonstrating a suppressed mineralisation of ecosystem-derived organic carbon in BC (biochar) amended soils (Wang et al., 2016; Cross and Sohi, 2011; Liang et al., 2010). In contrast, the addition of BC in the form of biochar did not affect the mineralisation of labile organic carbon. Similar results were found by other studies, where no significant effect on the soil organic carbon mineralisation was observed following biochar addition (Wang et al., 2016; Kuzyakov et al., 2009). To understand the mechanisms underpinning the differences between soot and biochar effect on labile organic carbon mineralisation, further research is needed. However, it has been suggested that the decrease in soil organic carbon mineralisation due to the sorption properties of BC could be associated with its more recalcitrant fractions (Whitman et al., 2015). This is also what our findings potentially suggest. The HyPy analyses on soot and biochar showed that soot was more stable under HyPy condition than biochar, with a larger recalcitrant fraction compared to biochar, 69% and 52%, respectively. Potentially suggesting that driving the differences between soot and biochar effect on organic carbon mineralisation might be the presence of a greater recalcitrant fraction in soot compared to biochar. However, further analysis is needed to investigate this hypothesis. Additionally, previous research has demonstrated that the suppression of soil organic carbon increases with increased biochar concentration (Liu et al., 2018). Particularly, in Liu et al. (2018) a significant

decrease in soil organic carbon mineralisation was observed only after biochar application rate of about 67 t ha^{-1} . Thus, explaining the differences between soot and biochar effect on soil organic carbon mineralisation might also be the rate of biochar applied in this experiment (10 t ha^{-1}). However, further research is needed to investigate this. While we show that soot influences the dynamics of labile carbon mineralisation, we have also demonstrated that it is mineralised itself and therefore represents a hitherto overlooked component of the carbon cycle. As suggested by Bird et al. (2015), BC degradation processes in soil can be seen as continuum ranging from more labile lightly charred materials to highly recalcitrant condensed aromatic molecule, although our analyses suggest that even at the recalcitrant end of this continuum a proportion of BC is still mineralizable over short time-scales. The chemical analysis of our labelled soot revealed that around 30% of the soot is potentially labile and composed of aromatic hydrocarbons, such as pyrene and phenanthrene, that are known to be readily mineralised by the soil microorganisms (Couling et al., 2010). These PAHs are still likely to represent the minor portion of the soot that was able to be mineralised over the course of the experiment (Couling et al., 2010). Our experimental results also indicated that soot mineralisation declined with time. While the mechanisms behind the decrease in soot mineralisation need further research, microbial toxicity induced by PAHs associated with soot could have played a role in the slowdown of the soot mineralisation (Patel et al., 2020). Similarly, soot addition could have caused a change in soil pH, unfavourable for soil microbes, thus changing their biomass, composition and activity and consequently reducing soot mineralisation (Thies et al., 2015; Lehmann et al., 2011).

Our research provided the first measure of the turnover of soot in terms of carbon cycling in soils, allowing us to measure mineralisation of soot, even in very small quantities for the first time. We estimated that the amount of carbon mineralised from soot over the course of the experiment is about 0.17%. Since small changes in TOC respiration can have significant impact on atmospheric CO_2 concentration (Davidson and Janssens, 2006; Schlesinger and Andrews, 2000), we contextualized this result, estimating both at global and European scale the amount of CO_2 related to the mineralisation of BC in form of soot. Global BC deposition rate are estimated to be of 17 Tg yr^{-1} (Bird et al., 2015), whereas European BC emission are estimated to be 470 Gg yr^{-1} (Bond et al., 2013). Considering a global land area of $149 \times 10^8 \text{ ha}$ (excluding ice areas) and a European land area of $10.18 \times 10^8 \text{ ha}$ we estimated that with mineralisation of 0.17% of BC per $\frac{1}{2}$ year would lead to approximately $27,576 \text{ ton of CO}_2 \text{ ha}^{-1} \frac{1}{2} \text{ yr}^{-1}$ and $0.0028 \text{ kg of CO}_2 \text{ ha}^{-1} \frac{1}{2} \text{ yr}^{-1}$ at global and European scale, respectively. To understand the magnitude of the contribution of the soot mineralisation to the global carbon cycle, considering that global emission from land use and land use

change are estimated to be about $5.2 \pm 2.6 \text{ Gt CO}_2 \text{ yr}^{-1}$ (IPCC, 2019), we estimated that BC mineralisation in form of soot contributes to about 0.040% of these emissions.

5. Conclusion

This research has demonstrated for the first time that BC in the form of soot suppresses the mineralisation of labile organic carbon in soils and that BC in the form of soot can be, to some extent, mineralised in soils contributing to soil CO_2 effluxes. This research has also shown that BC in the form of biochar has no effect on the mineralisation of labile organic carbon. These findings represent a step-change in understanding the influence of soot and other compounds on the BC continuum on carbon dynamics, providing compelling evidence that BC in the form of soot plays an active role in soil carbon dynamics. This has major consequences for the way we measure, monitor and manage soils for carbon storage and sequestration in the future. A priority for future research will be understanding which carbon pools in soils are affected by BC, for example, the influence of soot on the mineralisation of labile organic carbon in soils through rhizodeposition from plants (Hütsch et al., 2002), in addition to the microorganisms responsible for the mineralisation of BC itself in soils (Whitman et al., 2016). Further research is also needed to understand the mechanisms driving the differences between soot and biochar influence on the mineralisation of labile organic carbon.

CRediT authorship contribution statement

Marta Crispo: Conceptualization, Methodology, Data curation, Formal analysis, Investigation, Project administration, Visualization, Writing – original draft. **Duncan D. Cameron:** Conceptualization, Methodology, Formal analysis, Visualization, Funding acquisition, Writing – original draft. **Will Meredith:** Formal analysis, Writing – review & editing. **Aaron Eveleigh:** Formal analysis. **Nicos Ladommatos:** Formal analysis. **Ondřej Mašek:** Formal analysis, Writing – review & editing. **Jill L. Edmondson:** Conceptualization, Methodology, Validation, Resources, Funding acquisition, Supervision, Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.149659>.

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