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Stable polycyclic aromatic carbon (SPAC) formation in wildfire chars and engineered biochars

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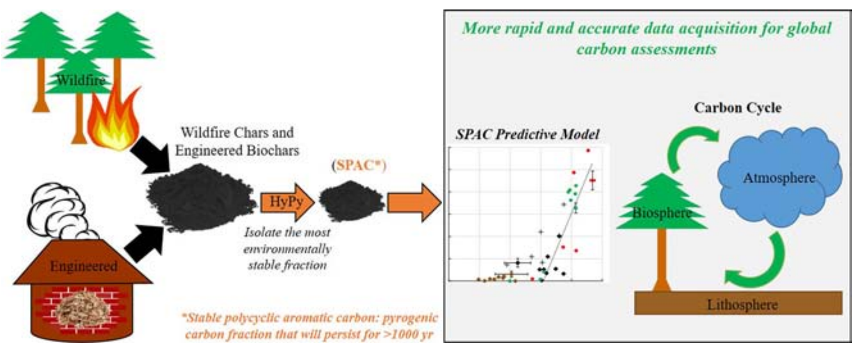
HIGHLIGHTS

- Wildfire chars and engineered biochars are important for the global carbon cycle.
- The stable polycyclic aromatic carbon (SPAC) fraction of chars is quantified.
- SPAC can persist in global environments for >1000 years.
- SPAC increases with pyrolysis severity and correlates with H:C, O:C, and mass loss.
- A SPAC predictive model is presented to improve carbon sequestration assessments.

GRAPHICAL ABSTRACT



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ABSTRACT

Pyrogenic carbon (PyC) is an important component of wildfire chars and engineered biochars due to its potential environmental longevity, the most environmentally stable fraction of which is called stable polycyclic aromatic carbon (SPAC) and is projected to persist in global environments for >1000 yr. Rigorous characterization of SPAC, whether formed in wildfires or engineered, is essential for accurate global carbon cycle models. However, the quantification of SPAC remains challenging and methods for its direct characterization are often inaccessible and/or highly specialized. Additionally, these methods often rely on SPAC formation measured in laboratory biochars produced in inert environments, which have been shown to correlate poorly with wildfire chars and/or engineered biochars manufactured in oxidative environments. The present study investigated the relationship between SPAC formation and physicochemical metrics - mass loss and molar H:C and O:C ratios - that capture the influences of multiple formation variables, including gas environment temperature, O_2 availability, and pyrolysis duration, and negates the need for these variables to be directly measured. SPAC content is measured in this study using hydrogen pyrolysis (HyPy), which is an established accurate method for characterizing that most environmentally stable PyC fraction. Results show that SPAC formation and elemental ratios correlate linearly with increased mass loss, which is reflective of increased pyrolysis severity. The relationship between these char characteristics allows for SPAC prediction based on measurement of mass loss during char formation, as well as the standardized elemental analysis method. In this study, wildfire chars exhibited relatively low SPAC contents of <30 wt% on a dry, ash-free basis, indicating that a significant fraction of PyC formed in these chars remains labile or semi-labile, while engineered biochars had a range of SPAC contents up to approximately 75 wt%. The predictive SPAC models developed in this work can improve global carbon accounting models.

1. Introduction

Pyrogenic carbon (PyC) is an important component in global and regional carbon dynamics (Santin et al., 2020; Landry and Matthews, 2017;

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Santín et al., 2016; Santín et al., 2015; Haig et al., 2020; Ascough et al., 2020). PyC is naturally formed from biomass that has undergone oxidative pyrolysis during wildfires, or it is engineered from biomass feedstocks via thermochemical treatments such as pyrolysis. Upon thermal treatment under these conditions, biomass is transformed into a carbon-rich char wherein the carbon in the biomass is rendered more environmentally stable and recalcitrant to biotic and abiotic decomposition (Bis et al., 2018; Hagemann et al., 2018; Spokas et al., 2012; Cheng et al., 2006; Zimmerman, 2010; Bruun et al., 2008; Leng et al., 2019). There has long been evidence that wildfire chars and cooking charcoal ashes from historical cultures persist in the environment (Ascough et al., 2009; Ascough et al., 2010a; Koele et al., 2017) as can be observed in the Terra Preta soils of the Amazonian Basin (Glaser et al., 2001), and PyC in wildfire chars and engineered biochars (together, "chars") has the potential to be sequestered without re-release to the atmosphere for centuries to millennia, depending on the formation and sequestration conditions (Spokas et al., 2012; Zimmerman, 2010; Leng et al., 2019). As a result, engineered production of PyC-containing biochar is now being targeted as a carbon dioxide removal (CDR) pathway for the long-term sequestration of atmospheric carbon (Leng et al., 2019; Chen et al., 2021; Minx, 2018), and the pool of PyC formed during wildfires is being re-evaluated in carbon models as a natural CDR mechanism (Santín et al., 2016; Santín et al., 2015; Ascough et al., 2016; Jones et al., 2019; Santín et al., 2017; Surawski et al., 2016).

Rigorous characterization of PyC stability and quantity, whether developed through wildfire or engineered, would improve projections of carbon sequestration longevity and improve critically needed estimates of global carbon fluxes and storage (Chen et al., 2021; Ascough et al., 2016; Ascough et al., 2010b; Belcher and Hudspith, 2016; Schneider et al., 2013; Joseph et al., 2021; Lian and Xing, 2017), but this remains challenging for several reasons. First, PyC is a continuum of carbonaceous chemical compounds varying considerably in aromaticity (Zimmerman and Mitra, 2017; Preston and Schmidt, 2006; Cotrufo et al., 2016) because the physical and chemical composition of PyC is highly dependent on its formation conditions, whether by wildfire (Ascough et al., 2010b; Belcher and Hudspith, 2016) or engineered (Santín et al., 2017; McParland et al., 2009; Leng and Huang, 2018; Soucémarianadin et al., 2013). Second, while production conditions, such as temperature, have been correlated to the stability of PyC (Ascough et al., 2010b; Schneider et al., 2013; McParland et al., 2009; Belcher et al., 2018; Ascough et al., 2011; Schneider et al., 2010; Guizani et al., 2019), the monitoring and quantification of these conditions can be problematic in both field and laboratory settings due to the difficulty and often impracticality of maintaining thermocouple contact with biomass during its conversion, particularly in oxidative environments (Shannon and Butler, 2003; Hindasageri et al., 2013). Lastly, the stability of PyC could theoretically be directly measured by quantifying the carbon remaining in situ year after year following wildfire char or engineered biochar deposition, but monitoring PyC over its projected lifetime of hundreds or thousands of years has practical challenges and requires the use of projective models (Leng et al., 2019; Kuzyakov et al., 2014; Weng et al., 2017).

A robust estimation of PyC stability could be accomplished by direct characterization of the carbon structure in wildfire chars and engineered biochars, but this is a challenging objective for a chemically complex material such as PyC (Leng et al., 2019; Zimmerman and Mitra, 2017; Preston and Schmidt, 2006; Cotrufo et al., 2016). Higher formation temperatures generally lead to more condensed aromatic PyC, which is associated with greater environmental persistence (Ascough et al., 2020; McParland et al., 2009). When biomass is exposed to increasingly higher temperatures in a limited oxidizer environment, its molecular structures are transformed into condensed benzene rings (250–300 °C) which fuse together into larger aromatic structures (>400 °C), eventually leading to the formation of a heterogeneous structure composed of micrographitic domains and other thermochemically altered material (Matosziuk et al., 2019; Bird et al., 2015). Two principal pathways have been identified for the transformation of raw biomass into these highly aromatic materials: first, the loss of labile organic species leads to an increasingly carbonaceous residue and, second, hydrocarbons from the gas phase re-condense onto the residue surfaces to increase the aromaticity of the PyC (Preston and Schmidt, 2006; Bird et al., 2015). Counteracting these formation pathways, PyC can be partially or completely consumed in oxidative conditions (Doerr et al., 2018; Santín et al., 2013). Importantly, while temperature has been found to have the greatest impact on final char properties and, thus, is typically used to describe the formation process, other production parameters, such as environment gas, residence time and heating rate, also contribute to final PyC characteristics (Ascough et al., 2010b; Schneider et al., 2013; McParland et al., 2009; Belcher et al., 2018; Ascough et al., 2011; Schneider et al., 2010). Thus, correlations of PyC stability with temperature alone are unable to capture the effects of these other variables which also strongly influence char properties (Santín et al., 2017; Belcher and Hudspith, 2016; Schneider et al., 2013; Spokas, 2010). The net result of these processes is that PyC can be found in an assortment of wildfire chars and engineered biochars with highly variable concentrations of PyC and PyC stabilities based on formation conditions (Santin et al., 2020; Bird et al., 2015), making the prediction and modeling of PyC stocks challenging.

Degree of aromaticity is an important PyC property because it is an indicator of the degree of thermal alteration and can be measured by quantifying the aromatic cluster size or the number of fused rings in wildfire chars and engineered biochars. The stable polycyclic aromatic carbon (SPAC) pool is composed of carbonaceous clusters with >7 fused rings, where the stability of the SPAC fraction is believed to be on centennial timescales or greater (Bird et al., 2015; McBeath et al., 2015; Rombolà et al., 2016; Rombolà et al., 2015). Rombolà et al. (Rombolà et al., 2016) characterized the molecular composition of identified labile and semi-labile fractions of biochars and observed polyaromatic hydrocarbons (PAHs) with 2 to 7 rings, alkylated derivatives up to C_4 and partially hydrogenated PAHs. Additionally, Rombolà et al. (Rombolà et al., 2015) investigated the fate of extracted PAHs with <7 rings and biochars in topsoils and observed significant losses of the PAHs during the 2 yr study, while the concentration of the SPAC fraction of the biochars did not change significantly. These findings and others indicate that chars with large fractions of these highly condensed aromatic clusters consisting of coronene (7 fused rings) and larger compounds will have the longest environmental stability (Leng et al., 2019; Ascough et al., 2009; Rombolà et al., 2016; Rombolà et al., 2015; Cao et al., 2012). Direct assessment of aromatic content has been proposed using a number of techniques, including thermal, chemical, optical, molecular marker and physical methods (Leng et al., 2019; Chen et al., 2021; Hammes et al., 2007). Among these, hydrogen pyrolysis (HyPy) has emerged as a favorable technique for accurately quantifying the SPAC fraction due to its ability to isolate a chemically well-defined polyaromatic structure with peri-condensed aromatic clusters of >7 rings (Haig et al., 2020; Ascough et al., 2009; Rombolà et al., 2016; Rombolà et al., 2015; Meredith et al., 2012). Thus, HyPy can be used to assess the SPAC portion of PyC that will endure on centennial time scales and greater, while the more labile and semi-labile content is susceptible to degradation and should not be considered part of long-term PyC stocks (Santin et al., 2020; Santín et al., 2016; Santín et al., 2015; Hagemann et al., 2018; Spokas et al., 2012; Leng et al., 2019; Jones et al., 2019).

Many of the aforementioned techniques for assessing SPAC contents are effort-intensive and require highly specialized equipment. Alternatively, more readily accessible analyses, such as elemental analysis to quantify carbon (C), hydrogen (H), and oxygen (O) contents of chars, are often used and results have been correlated with projected char carbon lifetimes. Incubation studies of up to approximately a decade have been conducted (Kuzyakov et al., 2014; Weng et al., 2017; Cao et al., 2012), and the stability of PyC in these experiments has been correlated with a number of char properties including O:C and H:C molar ratios. As a result of these studies and correlations, chars with molar $O:C < 0.2$ have been estimated to have half-lives >1000 yr and chars with molar $H:C < 0.7$ and $O:C < 0.6$ have been estimated to have half-lives of at least 100 yr (Spokas et al., 2012; Santín et al., 2017; Budai et al., 2013). However, because the molecular composition of PyC exists along a continuum of carbonaceous species, some fraction of chars with low H:C and O:C ratios is still labile and more susceptible to degradation than the SPAC fraction of that same char.

Different model approaches have been proposed to address these different levels of carbon pool stability within chars, but these environment residence times are estimations and significant uncertainty remains.

In an effort to better forecast the environmental stability of wildfire chars and engineered biochars, there have been attempts to study laboratory-produced chars and relate their properties to pyrolysis parameters, as well as reverse engineer formation conditions of chars produced during wildfires (Santín et al., 2017; Belcher and Hudspith, 2016; Schneider et al., 2013; Schneider et al., 2010; Wurster et al., 2013). Errors in the assumption that laboratory chars produced in inert environments can represent wildfire-derived chars have been identified by Santín et al. (Santín et al., 2017) and others (Belcher and Hudspith, 2016; Schneider et al., 2013; Spokas, 2010), with the recommendation that laboratory chars be manufactured under more representative oxidative conditions. However, the classification of wildfire chars and engineered biochars based on formation parameters such as gas environment temperature, pyrolysis time, and O_2 availability is challenging because of the highly complex and variable environments under which pyrolysis may occur (Ascough et al., 2020; Santín et al., 2017; Schneider et al., 2013; McBeath et al., 2013). For example, wildfire formation conditions fluctuate significantly in space and time, so a singular residence time, temperature, or oxygen (O_2) environment will not accurately capture the formation conditions experienced by the chars that remain after the fire has passed (Santín et al., 2017; Belcher and Hudspith, 2016). Some similar variability may be experienced by engineered biochars, particularly those manufactured in incompletely inert environments, introducing similar challenges in characterization.

The study presented herein conducted extensive characterization of wildfire chars and engineered biochars to relate the SPAC fraction of these chars to readily measurable properties, namely mass loss and molar O:C and H:C ratios. The metrics of mass loss and molar O:C and H:C were selected to capture overall pyrolysis severity induced by combined influences of gas environment temperature, pyrolysis duration, and O_2 availability during pyrolysis. Engineered biochars were produced in a systematic laboratory investigation of formation conditions that included variation of gas environment temperature, pyrolysis duration, and O_2 availability. Results were analyzed together with wildfire chars formed during the 2020 Mullen Fire (MF) in the Medicine Bow-Routt National Forest in southeastern WY, USA, for which the exact local temperature, pyrolysis duration, and O_2 availability during pyrolysis are unknown due to the challenges of measuring these parameters in wildfires. The investigated feedstock for both engineered biochars and wildfire chars was lodgepole pine (*Pinus contorta*) bark/cambium from healthy pine (HP) or bark beetle-killed pine (BK). Mass loss was measured for all engineered biochars and was estimated for wildfire chars. Elemental analysis and HyPy were used to characterize the physicochemical properties of all wildfire char and engineered biochar samples, and correlations between elemental composition, mass loss, and SPAC content as determined by HyPy were investigated. The findings of this work can be used to estimate the SPAC fractions of chars formed during wildfires or engineered, such as for CDR, without needing precise knowledge of the production conditions or full-scale field studies after char deposition events, thereby significantly improving estimations of SPAC for global carbon accounting.

2. Materials and methods

2.1. Chars

2.1.1. Wildfire-generated chars

Wildfire chars were collected from the Mullen Fire (MF) which impacted 176,878 acres of the Medicine Bow-Routt National Forest in southeastern WY, USA from mid-September to early November 2020 (Mullen Fire, 2020). This wildfire burned through a densely vegetated lodgepole pine forest that was in standing-dead and deadfall stages of the mountain bark beetle (*Dendroctonus ponderosae*) epidemic affecting the region (Berner et al., 2012; Harvey et al., 2014; Kayes and Tinker, 2012; Reed et al., 2014). Standing healthy pine (HP) and beetle-killed pine (BK) boles were collected in mid-December of 2020 with a sample collection strategy based on a previous study (Howell et al., 2021), where the bark/cambium was identified as the primary source of PyC in standing timber post-fire and is therefore isolated from the rest of the pine boles after collection. Notably, the MF burned in a fuel complex very similar and in close proximity to the forest impacted by the 2018 Badger Creek Fire (BCF) investigated in Howell et al. (2021). Thus, boles were collected from essentially the same fuel complex as that investigated in Howell et al. (2021).

MF samples were collected near Fox Park, WY. HP and BK bole cross-sections were collected from two site types: unburned and burned. The burned sites were visually selected based on complete charring of the boles from the base to the former canopy height to distinguish it from surface fire sites where the canopy was still intact but with the foliage orange and dead. All burned HP and BK boles were collected within approximately 75 yards of each other, and the unburned HP and BK boles were collected just outside the fire boundary, approximately 200 yards from the burned sample site.

A total of 6 burned boles were selected and felled: three replicates each for burned HP and burned BK. Less variability in unburned boles was expected based on previous work (Howell et al., 2021), and preliminary testing was used to assess the required number of replicates for unburned HP and unburned BK. Proximate analysis, described in detail in Section 2.2, was used to compare unburned HP and BK, and results are provided in Supplementary Material. Based upon the results, the fuel properties of the unburned HP and BK bark/cambium collected for this study were determined to be very similar to those investigated previously (Howell et al., 2021). As a result, one bole each of unburned HP and unburned BK was deemed sufficient for the physicochemical analysis undertaken in the present study. A permit was obtained for the only live tree felled, the unburned HP (Laramie Ranger District, reservation no. 0355328730-1).

Differences in charring depth with position along bole length were observed in burned HP and BK boles and, thus, char samples were collected from several locations along the bole lengths to assess variability in charring extent and severity within a bole. Trees were felled using a cut approximately half a meter from the ground, and all ensuing measurements were made from the cut ends of the felled boles. Cross-sections were cut at 1 to 4 m from the base, in 1-m increments, and at 8 m from the cut end for an investigation of fire effects on char properties with respect to vertical location during the MF. The total number of cross-sections collected for analysis resulted in 70 samples. All bole sections were dried for a minimum of 24 h at 100 °C and the bark/cambium was then removed, pulverized, and sieved to <425 μm. Notably, preliminary analysis showed negligible statistical differences in physicochemical properties measured for whole bark/cambium particles and pulverized samples.

Again using proximate analysis to conduct preliminary assessment of the samples, bark/cambium was found to differ negligibly with bole length from 1 to 4 m in unburned and burned bark/cambium (results provided in Supplementary Material). Based on this finding, the wildfire chars selected for further study were reduced to bark/cambium samples from the base, 2 m from the base (diameter at breast height, DBH), and 8 m from the base (crown). The reduced matrix of wildfire char samples used for the remainder of the study is shown in Fig. 1. Further preliminary proximate analysis of the wildfire chars from each bole at each location along the bole height showed that properties differed significantly between boles, particularly in the burned BK (Supplementary Material). Thus, samples at each tested location along each bole were kept separate for each bole to capture the variability in chars collected from unique trees, each of which burned relatively close to each other but which nevertheless likely experienced different heating and oxidative conditions.

2.1.2. Laboratory-engineered chars

Engineered biochars were produced in the laboratory under a variety of gas environment temperature, pyrolysis duration, and O_2 availability conditions to generate biochars over a wide range of pyrolysis severities resulting from the overall influences of these combined pyrolysis parameters. Unburned HP bark/cambium, pulverized to < 425 μm, was the feedstock

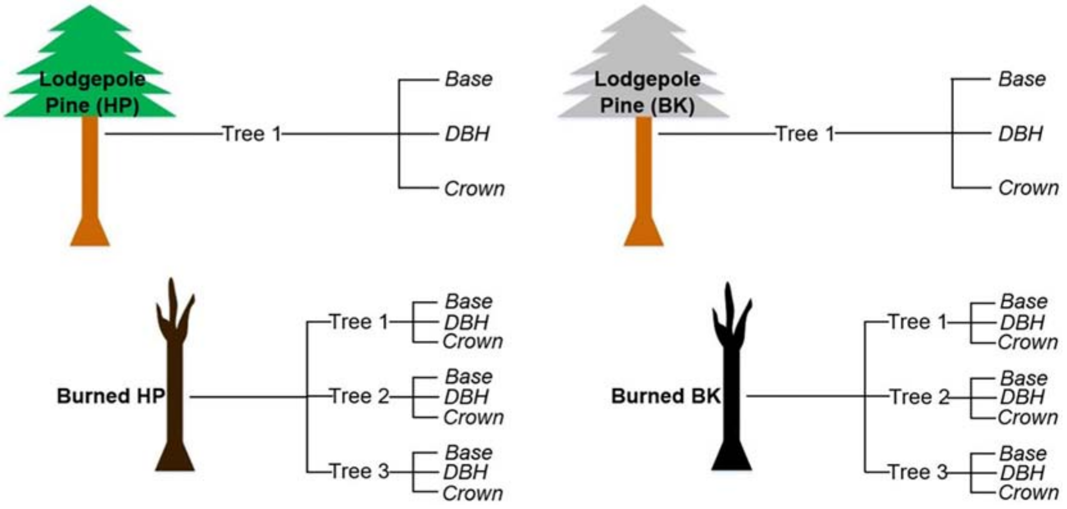

Fig. 1. Summary of bark/cambium samples collected from the Mullen Fire and analyzed in this study. Bark/cambium samples from the base, diameter at breast height (DBH), and the crown of unburned and burned healthy (HP) and beetle-killed (BK) trees were investigated. Burned HP and BK chars comprise the wildfire chars characterized in this study.

used to produce biochars using a TA Instruments Q500 thermogravimetric analyzer (TGA). The pyrolysis condition test matrix is shown in Fig. 2. Three gas environments were chosen to investigate impacts of O_2 (purity 99.9 %) availability on biochar properties: 1) N_2 (purity 99.99 %), 2) 95/5 vol/vol% N_2/O_2, and 3) 80/20 vol/vol% N_2/O_2, with appropriate TGA calibrations performed for each gas environment. The gas environments were chosen to mimic O_2 availability scenarios in which: 1) no O_2 is present, 2) limited O_2 (5 vol%) is available, and 3) O_2 availability is not limited and biochar is formed in an air environment. Three maximum gas temperatures of 300, 550, and 800 °C, and three durations of 1, 5, and 10 min at those maximum temperatures were tested for each of the three environment gases. Additionally, mildly charred HP bark/cambium was produced at 200 °C and over the same range of pyrolysis durations to explore the effect of low severity thermal treatment. Biochars manufactured at 200 °C were only produced in an N_2 gas environment due to minimal expected impacts of oxidation at that temperature. In total, 30 different biochars were systematically produced to explore influences of pyrolysis severity on SPAC formation, and to capture a wide range of environment conditions that may be experienced by lodgepole pine bark/cambium during wildfires and engineered biochar production for CDR.

The TGA method used to manufacture biochars began with a drying step in which approximately 100 mg of HP bark/cambium sample was ramped at 20 °C/min and held at 100 °C for 10 min. After drying, the sample was heated at 100 °C/min to a maximum temperature of 200, 300, 550, or 800 °C. Following the ramp to the desired temperature, the bark/cambium sample was held isothermal for one of three durations: 1, 5, or 10 min. All drying, ramping and isothermal stages were conducted in the respective gas environment for each test (N_2, limited O_2, or air). At the end of the isothermal step at the peak temperature, the TGA furnace gas environment was switched to N_2, if this was not already the environment gas, and cooled to 90 °C before the biochar product was unloaded from the TGA furnace in order to prevent any oxidation of the biochar during cooling. A total gas

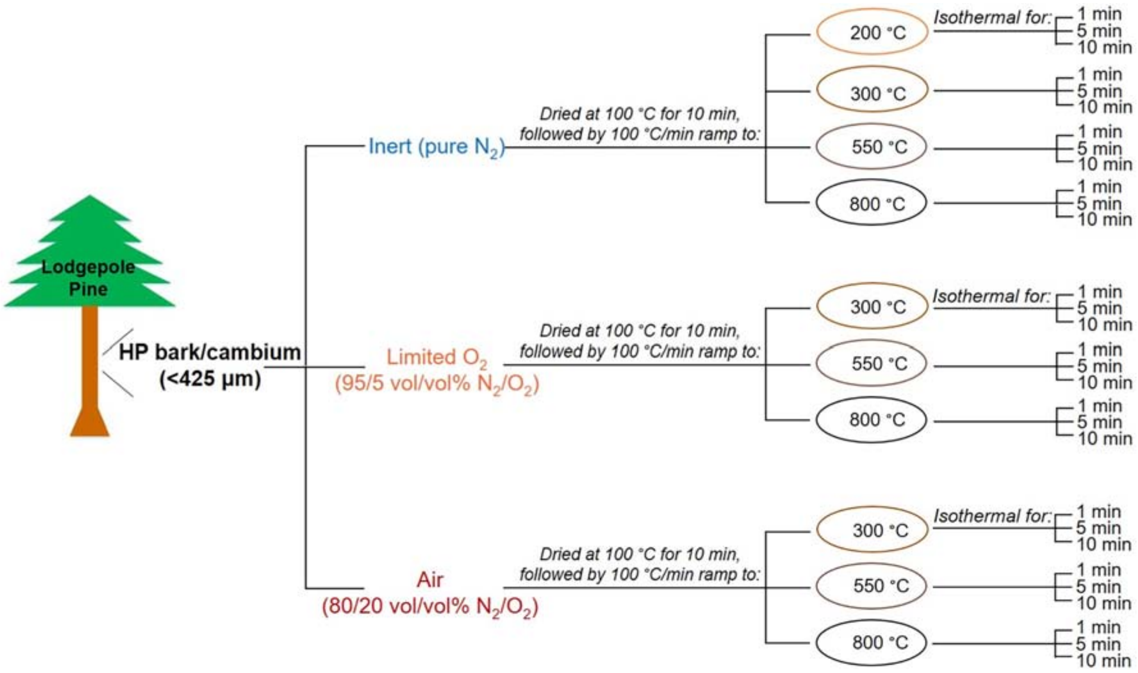

Fig. 2. Pyrolysis condition test matrix for engineered biochars produced in the laboratory from unburned healthy pine (HP) bark/cambium.

flow rate of 100 mL/min was maintained through the TGA furnace throughout the tests. This biochar production method was repeated for each pyrolysis condition until sufficient sample was acquired for ensuing proximate (Section 2.2), elemental (Section 2.3), and hydrogen pyrolysis (Section 2.4) analyses.

Importantly, the biochars manufactured at 550 and 800 °C in oxidative gas environments likely experienced significantly higher temperatures than the gas temperatures reported by the TGA due to oxidation at the biochar surfaces. The maximum char temperature is not measured within the TGA, therefore the biochars produced in the two oxidative conditions investigated in this study are defined by the maximum gas temperature measured by the TGA.

2.2. Proximate analysis

Proximate analysis was performed on all wildfire chars and engineered biochars using a TA Instruments Q500 TGA following the procedure outlined in (Howell et al., 2021). Briefly, the procedure consists of drying and pyrolysis in N_2, followed by oxidation in an 80/20 vol/vol% N_2/O_2 furnace gas environment. In N_2, the wildfire char or engineered biochar sample is ramped to 100 °C at 20 °C/min and held isothermal to dry for 10 min, followed by a 40 °C/min ramp to 950 °C where the sample is held isothermal to pyrolyze for 7 min. The mass loss during the drying step is the moisture content (MC) of the wildfire char or engineered biochar, and the mass loss during the pyrolysis step is the volatile content (VC). After the pyrolysis step, the sample is cooled to 750 °C and O_2 is introduced to the furnace in an 80/20 vol/vol% N_2/O_2 mixture to oxidize the remaining fixed carbon (FC). The final mass remaining after this FC burnout is the ash content (AC), and the FC content can be determined by difference based on the initial sample mass, MC, VC, and AC. The total gas flow rate during the proximate analysis procedure was maintained at 100 mL/min. Char sample sizes of approximately 5 mg were used for all proximate analyses. After preliminary proximate analyses conducted using four replicates of engineered biochars revealed negligible statistical differences (Supplementary Materials), two replicates of each wildfire char and engineered biochar outlined in Figs. 1 and 2 underwent proximate analysis, and uncertainty was determined as standard deviation between the two replicates.

2.3. Elemental analysis

A Thermo Scientific Flash*Smart* Elemental Analyzer (EA) was used to obtain the CHNS composition of the wildfire chars and engineered biochars. The 2,5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene (BBOT) standard was used following the Classic Organic Elemental Analysis method (Krotz et al., nd). Standards were massed for 2, 2.5, and 3 mg for calibration, and samples were prepared within this calibration mass range. The CHNS contents of the chars were directly measured on a mass basis using the EA, while O content was determined by difference following ASTM D3176-15 (ASTM, 2013). Two EA replicates were performed on each char, and uncertainty was assessed using standard deviation.

2.4. Hydrogen pyrolysis

Isolation of the SPAC content of engineered biochars and wildfire chars was achieved using the HyPy technique developed in (Ascough et al., 2009; Meredith et al., 2012) and utilized in (Howell et al., 2021). In brief, chars were prepared with ammonium tetrathiomolybdate ($(NH_4)_2MoS_4$) such that, after HyPy treatment, dispersed sulphided molybdenum (Mo) catalyst would comprise 5 wt% of the sample. The samples were primed with the Mo catalyst precursor using a 1:1 deionized water/methanol solvent where $(NH_4)_2MoS_4$ was 0.1 M in the solvent solution. Following Mo precursor loading, samples were vacuum dried at 60 °C for a minimum of 24 h and stored at 4 °C in N_2 until HyPy treatment.

Three Mo precursor-primed char samples packed into separate quartz tubes were loaded into a 300 mm-long, 12.5 mm-diameter stainless steel reactor per HyPy treatment. A thermocouple was inserted into the center of the reactor to monitor sample temperature during HyPy treatment. Samples loaded into the HyPy reactor were first purged in N_2 at 15 MPa to remove air from the reactor system and prevent oxidation during the HyPy treatment. After purging, the HyPy reactor was flushed in hydrogen (H_2, purity 99.99 %) at 15 MPa and with a flow rate of 1.5 SLPM. The HyPy treatment was then initiated by ramping the sample temperature from 50 to 300 °C at 100 °C/min, followed by a ramp to 550 °C at 10 °C/min. At 550 °C, the samples were held isothermal for 5 min. The combination of high-pressure H_2 and Mo catalyst enables the liberation of labile carbonaceous species without allowing the evolved species to re-condense onto available aromatic surfaces, effectively isolating the SPAC within the chars that was formed during the original fire event or laboratory production (Haig et al., 2020; Ascough et al., 2009; Preston and Schmidt, 2006). Two HyPy replicates were performed on each of the chars, and replicates of a given sample type were then composited for further analysis post-HyPy. Post-HyPy residues were stored at 4 °C in N_2 until further analysis.

Following HyPy treatment and reduction of the char samples to SPAC content, mineral content, and ash, the SPAC content was assessed using a modified proximate analysis combined with elemental analysis. Proximate analysis of post-HyPy residues was conducted using the following TGA technique. In N_2, post-HyPy residues were dried at 100 °C for 10 min, followed by a ramp of 100 °C/min to 300 °C and 10 °C/min to 550 °C. After an isothermal step at 550 °C for 5 min, O_2 was introduced to the TGA furnace at 20/80 vol/vol% O_2/N_2 to oxidize the remaining FC content. This proximate technique was modified from the proximate technique used to evaluate chars (Section 2.2) in order to mimic the HyPy thermal treatment after additional testing revealed that post-HyPy residues experienced negligible mass loss between 550 and 950 °C. Post-HyPy residues were also subjected to elemental analysis following the procedure described in Section 2.3. Two replicates of both the modified proximate and elemental analyses were performed on composited post-HyPy residues, and uncertainty was assessed by standard deviation. Combining the results of the post-HyPy modified proximate and elemental analyses, the dry, ash-free (DAF) basis SPAC (wt%) of the original wildfire chars and engineered biochars were determined using Eq. (1):

$$SPAC = C_{\text{HyPy residue}} * \frac{AC_{\text{preHyPy}}}{AC_{\text{HyPy residue}}} * \left(\frac{100}{100 - AC_{preHyPy}}\right) \quad (wt\%DAF) \qquad (1)$$

where $C_{\text{HyPy residue}}$, $AC_{\text{HyPy residue}}$ and AC_{preHyPy} are the C and AC of the post-HyPy residue, and the AC of the Mo-loaded pre-HyPy char sample, respectively, all in dry wt%. A relation between the C and FC of each post-HyPy residue was developed to reduce the number of elemental analyses required. Data from (Howell et al., 2021) and a subset of post-HyPy residues from this study consisting of three samples each of burned HP and burned BK chars, and three samples each from engineered biochars produced in N_2 and air, were selected to determine a linear relationship between post-HyPy FC and C on a dry basis (Supplementary Material). Once this linear relationship was established, the C of the other post-HyPy residues could be estimated using measured FC values of the post-HyPy residues. Lastly, SPAC values were corrected for small amounts of SPAC formed in unburned HP and BK during HyPy that are unavoidable during the HyPy procedure (Howell et al., 2021).

3. Results and discussion

3.1. Char mass loss

Proximate and elemental analyses of unburned HP and BK bark/cambium are provided in Supplementary Material on dry and DAF bases. The TGA mass loss profiles of the engineered biochars during production are shown in Fig. 3 for the biochars produced in N_2, limited O_2, and air, and at 300, 550, and 800 °C for 1, 5, and 10 min. Biochars manufactured in N_2 at 200 °C for 1, 5, and 10 min are also shown in Fig. 3a. Treatment temperature had the greatest impact on mass loss but greater treatment duration and oxidative gas environments also enhanced mass loss, highlighting the limitations of correlating

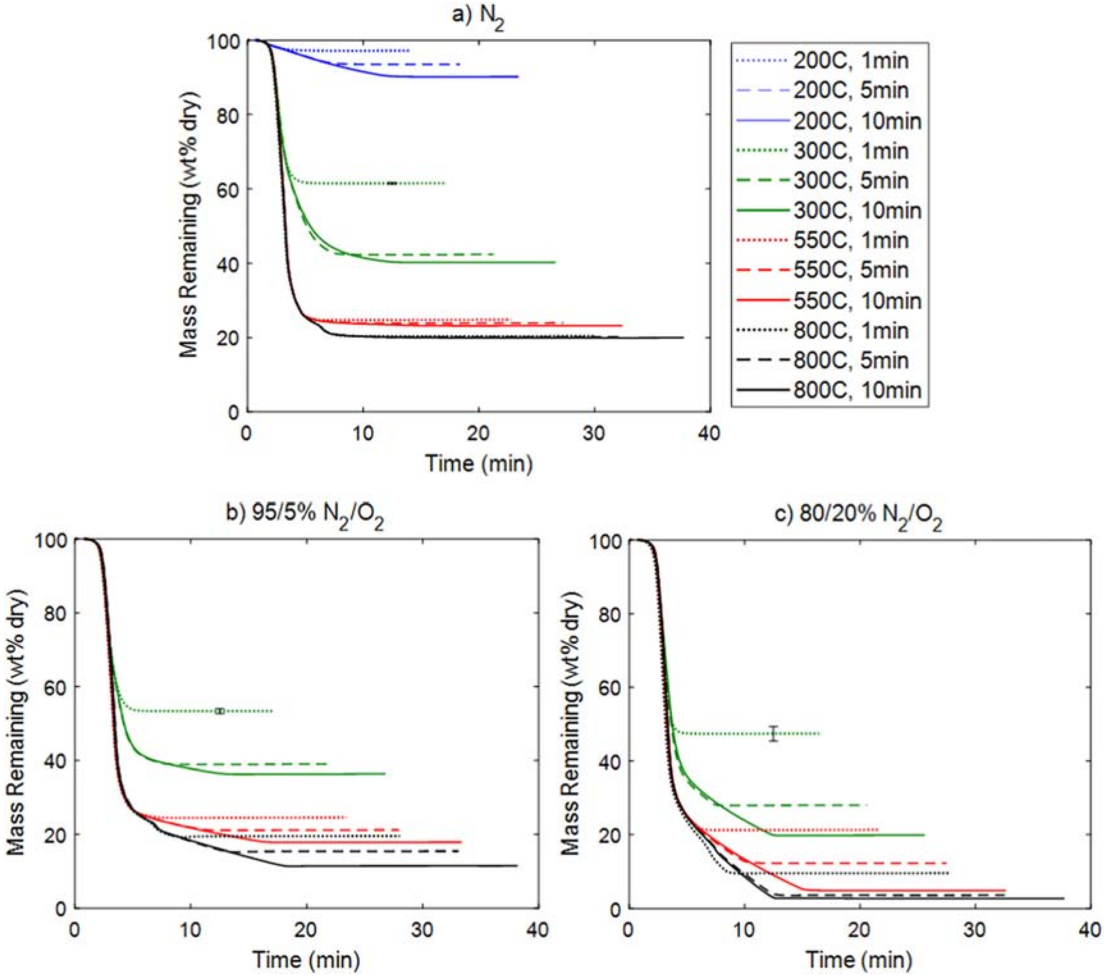

Fig. 3. Mass loss profiles of healthy pine (HP) bark/cambium during manufacture of engineered biochars in a) N_2, b) limited O_2, and c) air. Green profiles show the mass loss for samples treated at 300 °C, red profiles for samples treated at 550 °C, black profiles for samples treated at 800 °C, and blue profiles for samples treated at 200 °C (performed in N_2 (a) only). Dotted lines indicate treatments with a 1 min isothermal step at the maximum treatment temperature, while dashed lines indicate 5 min, and solid lines indicate 10 min. All results are wt% on a dry basis. Uncertainties are presented as averages for each gas environment category.

SPAC formation with any of these variables alone. In N_2 (Fig. 3a), the mass loss in the most severe thermal treatments (800 °C) reached a limit of approximately 80 % of the original mass on a dry basis, which is equivalent to the dry basis VC of the HP bark/cambium (Table S1, Supplementary Material) and indicates a fully pyrolyzed biochar reduced to FC and AC. In limited O_2 (Fig. 3b) and air (Fig. 3c), the FC of the HP bark/cambium underwent oxidation, resulting in greater mass loss than in an inert environment due to partial consumption of the biochar formed during pyrolysis. In limited O_2 (Fig. 3b), approximately 10 wt% of the original dry biomass remained after the most severe treatment at 800 °C and 10 min in that gas environment. The biochars manufactured under the most severe treatment conditions of 550 °C for 10 min and 800 °C for 5 and 10 min in air (Fig. 3c) experienced complete oxidation with only ash remaining at the end of the TGA treatment, and these biochars were eliminated from ensuing proximate, elemental and HyPy analyses due to the near or complete consumption of any potential SPAC.

The mass lost from bark/cambium during production of the engineered biochars was directly measured from the results shown in Fig. 3, but the mass lost during production of the wildfire-formed chars had to be estimated from unburned and burned bark/cambium samples. Mass loss was estimated using the difference in density between HP or BK wildfire chars and unburned HP or BK bark/cambium counterparts. Unground samples of each bark/cambium wildfire char, radially inclusive of the interior of the cambium to the exterior of the bark, were measured for radial thickness and imaged using ImageJ (Rasband, nd) to estimate particle areas. Particle volumes were then calculated, the mass of each particle was measured, and particle densities were calculated. Based on an assumption of negligible volume change upon charring, validated in preliminary testing which showed that particle dimensions changed by <1 % for an unburned bark/cambium particle subjected to an oxidative pyrolysis treatment, bark/cambium mass loss upon charring was estimated using the reduction in density (DAF basis) between unburned and burned samples. The mass losses experienced by the engineered biochars (Fig. 3) were generally similar to the range of mass losses estimated for the wildfire chars, and results are compared in Table 1.

Engineered biochars exhibited expected mass loss trends, with increased mass loss occurring at higher temperatures, longer treatment times, and with the addition of O_2. Increased severity of treatment is reflected in greater amounts of mass loss, with the most severe treatments being those treated to 550 °C for 10 min and 800 °C for 5 and 10 min in the air environment, which experienced total mass loss. The wildfire chars exhibited no consistent trends in mass loss behavior with location along the bole length. This variability can be seen in a comparison of the results from three different HP or BK trees in Table 1. The boles likely experienced different localized oxidative conditions during and following the fire due to the natural variability of wildfires, leading to variable resultant bark/cambium char properties, including mass loss. Such heterogeneous fire conditions are challenging to model and replicate, highlighting the difficulty of representing such chars with engineered biochars (Santín et al., 2017; Belcher and Hudspith, 2016; Schneider et al., 2013; Spokas, 2010). Additionally, and consistent with findings from (Howell et al., 2021), BK

Table 1

Mass loss (wt% dry, ash-free basis) induced by wildfire or laboratory pyrolysis and as measured for engineered biochars and estimated for wildfire chars. Average uncertainties for the wildfire chars and engineered biochars were ± 9.6 and 1.0 wt%, respectively.

Wildfire chars mass loss			Engineered biochars mass loss			
	HP	BK		N_2	95/5 % N_2/O_2	80/20 % N_2/O_2
			200 °C			
			1 min	2.92	–	–
			5 min	6.72	–	–
			10 min	10.2	–	–
Tree 1			300 °C			
Base	40.9	44.9	*1 min*	39.9	48.3	54.4
DBH	23.4	60.5	*5 min*	59.7	63.2	74.5
Crown	35.4	59.3	*10 min*	61.9	65.9	83.0
Tree 2			550 °C			
Base	36.0	72.0	*1 min*	77.9	78.1	81.5
DBH	29.8	74.8	*5 min*	78.8	81.6	90.8
Crown	32.5	62.0	*10 min*	79.5	85.1	98.5
Tree 3			800 °C			
Base	19.5	64.5	*1 min*	82.4	83.3	93.6
DBH	26.9	63.6	*5 min*	82.7	87.5	99.8
Crown	43.4	69.7	*10 min*	82.9	91.6	100

wildfire chars were found to have experienced greater mass loss upon charring than HP wildfire chars, suggesting that BK boles were less resistant to heating and charring than HP during the MF.

The FC and VC of the wildfire chars and engineered biochars are summarized in Table 2 on a DAF basis, and the results further emphasize the role of multiple environmental parameters on overall pyrolysis severity and final char properties. The FC and VC of the wildfire chars exhibit no consistent trends with respect to location along bole length and vary among boles, although the BK chars generally show greater amounts of FC than HP chars. Engineered biochars produced in N_2 displayed expected results based on pyrolysis severity in an inert gas environment: VC decreased and FC increased with increased temperature. However, upon addition of O_2 to the gas environment, the dependence of biochar VC and FC on gas environment temperature, treatment duration, and/or O_2 availability became complicated to isolate due to these multiple influences. In oxidative environments, the biochar formed during pyrolysis simultaneously oxidized, leading to associated heat release and elevated localized temperatures which support further pyrolysis and oxidation of the biomass. Thus, the results summarized in Tables 1 and 2 highlight the challenges of using only one formation parameter, such as pyrolysis temperature, for the characterization of char properties and show the importance of accounting for multiple formation parameters when investigating SPAC formation. Results suggest the need for metrics that embody the influences of all formation process parameters and capture overall pyrolysis severity as determined by the combined influences of gas environment temperature, treatment duration, and O_2 availability. Mass loss and molar H:C and O:C ratios were investigated in this study as such metrics, and results are presented in the ensuing sections.

Table 2

Fixed carbon content (FC) and volatile content (VC) of wildfire chars and engineered biochars. All results are wt% on a dry, ash-free basis. Average uncertainties of wildfire char and engineered biochar VC were ± 1.7 and 1.4 wt%, respectively. Average uncertainties of wildfire char and engineered biochar FC were ± 1.6 and 1.9 wt%, respectively.

Wildfire chars					Engineered biochars						
	HP		BK			N_2		95/5 % N_2/O_2		80/20 % N_2/O_2	
	VC	FC	VC	FC		VC	FC	VC	FC	VC	FC
					200C						
					1 min	89.2	10.8	–	–	–	–
					5 min	90.2	9.80	–	–	–	–
					10 min	87.7	12.3	–	–	–	–
Tree 1					300C						
Base	74.2	25.8	42.9	57.1	*1 min*	73.7	26.3	78.7	21.3	62.0	38.0
DBH	79.4	20.6	70.2	29.8	*5 min*	57.5	42.5	55.9	44.1	45.8	54.2
Crown	82.7	18.3	30.7	69.3	*10 min*	54.5	45.5	50.6	49.4	49.3	50.7
Tree 2					550C						
Base	69.9	30.1	31.0	69.0	*1 min*	26.3	73.7	31.5	68.5	28.7	71.3
DBH	85.6	14.4	51.3	48.7	*5 min*	23.4	76.6	35.4	64.6	30.9	69.1
Crown	79.3	20.7	34.6	65.4	*10 min*	21.9	78.1	33.2	66.8	–	–
Tree 3					800C						
Base	79.4	20.6	51.1	48.9	*1 min*	14.7	85.3	23.8	76.2	13.3	86.7
DBH	81.7	18.3	47.3	52.7	*5 min*	15.2	84.8	29.2	70.8	–	–
Crown	85.3	14.7	44.2	55.8	*10 min*	13.5	86.5	23.1	76.9	–	–

3.2. Relation of H:C and O:C to mass loss

The evolution of chemical composition with pyrolysis severity was assessed by quantifying the variation of H:C and O:C molar ratios with respect to mass loss for all wildfire chars and engineered biochars, and the results are shown in Fig. 4. The elemental data used to determine the molar H:C and O:C ratios in Fig. 4 are provided in Supplementary Material. As mass loss increases, H:C (Fig. 4a) and O:C (Fig. 4b) molar ratios decrease approximately linearly among all the chars regardless of pyrolysis gas environment temperature, duration, and O_2 availability, as well as wildfire versus laboratory production, and intact versus pulverized bark/cambium. Trendlines were fitted to all wildfire char and engineered biochar data points except the biochars manufactured in N_2 at 200 °C due to the lack of significant change in H:C and O:C for these biochars from the unburned HP bark/cambium sample, also shown in Fig. 4. Relationships between molar H:C and O:C and mass loss were determined through fitting of linear trendlines to be

$$H : C = -0.019 * \mathit{Mass\ Loss}\ (\mathit{wt\%DAF}) + 1.92 \tag{2}$$

and

$$O : C = -0.008 * \mathit{Mass\ Loss}\ (\mathit{wt\%DAF}) + 0.74. \tag{3}$$

The linear regression, R^2, of these trendlines in Fig. 4a (H:C) and Fig. 4b (O:C) were 0.89 and 0.83, respectively. Despite being formed over a wide range of gas environment temperatures, pyrolysis durations, and O_2 availabilities, the strong correlation of H:C and O:C with mass loss shows that final H:C and O:C properties can be predicted using mass loss as a severity indicator, regardless of the formation pathway experienced by a char.

HP wildfire chars underwent less severe mass loss than BK wildfire chars and, as a result, HP wildfire chars are primarily clustered around higher H:C and O:C molar values, while BK wildfire chars are located at lower H:C and O:C molar values, a finding that is consistent with those observed in (Howell et al., 2021) where charring was found to be greater in BK than HP. Many of the HP chars lost < 40 wt% of their mass, and results suggest that they underwent less severe pyrolysis than even the nearest N_2 engineered biochar manufactured at 300 °C, which lost 40 wt% of its original mass, as assessed by mass loss and H:C and O:C. Many of the wildfire chars with H:C and O:C molar ratios greater than those of that 300 °C N_2 biochar do not show a significant difference in molar H:C and O:C from unburned HP bark/cambium. This is an expected trend for biomass feedstocks, which have been shown to not undergo significant changes in H:C and O:C molar ratios until treatment temperatures exceed 200 °C; once temperatures > 200 °C are reached, molar O is lost at approximately twice the rate of H, corresponding to a greater rate of decrease in molar O:C (Weber and Quicker, 2018), as observed in Fig. 4. However, the results of the present study suggest that a maximum temperature experienced by HP chars cannot be deduced from the H:C and O:C or mass loss alone. Rather, the combined effects of gas environment temperature, O_2 availability in the gas environment, pyrolysis duration, and other factors likely contributed to the relatively mild pyrolysis severity observed in these wildfire chars.

While this study focused on bark/cambium, a comparison with other lignocellulosic fuels was made to assess the more general applicability of the linearly correlated results. Mass loss and H:C and O:C molar ratio data from Santín et al. (2017) and Ivanovski et al. (2021) were compared to

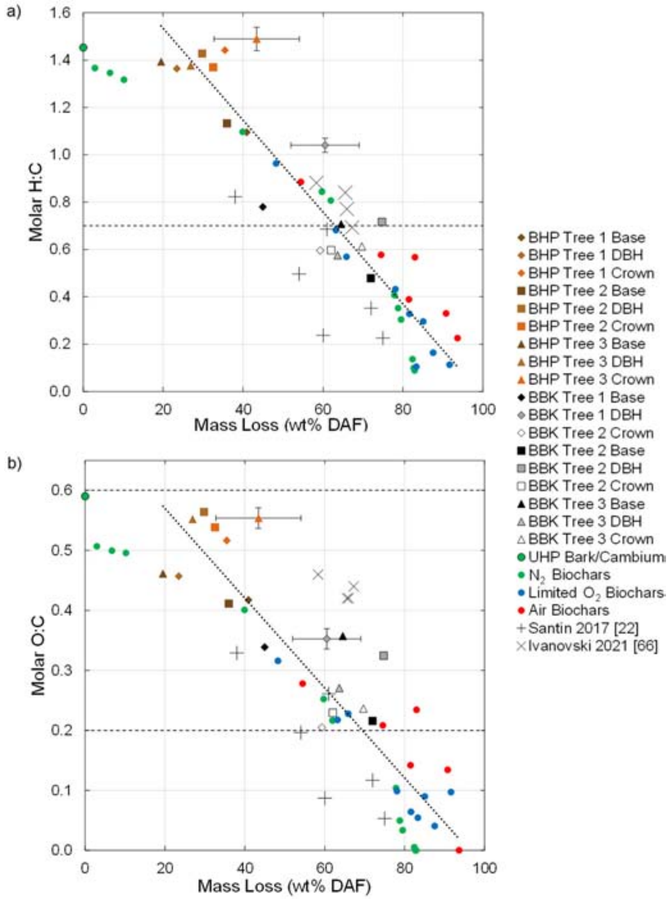

Fig. 4. a) H:C and b) O:C molar ratios with respect to mass loss (wt% dry, ash-free (DAF) basis) as measured and estimated for engineered biochars and HP and BK wildfire chars, respectively. Wildfire chars are shown in three shades of brown for the three burned healthy pine (BHP) bole repeats and three shades of black/grey for the three burned beetle-killed (BBK) bole repeats. BHP and BBK base samples are represented by diamond markers, BHP and BBK diameter at breast height (DBH) samples by square markers, and BHP and BBK crown samples by triangle markers. Engineered chars are represented as circular markers with samples produced in N_2 shown in green, limited O_2 in blue, and air in red. The unburned HP (UHP) bark/cambium sample used to manufacture all engineered chars is also shown for reference. Mass loss and H:C and O:C molar ratio data from Santín et al. (2017) and Ivanovski et al. (2021) are also presented as "+" and "x" markers, respectively. The molar H:C value of 0.7 and O:C values of 0.6 and 0.2 that have been correlated with projected biochar carbon environmental persistence of >100 and 1000 yr (Spokas et al., 2012; Budai et al., 2013) are identified using horizontal dashed lines. Linear trendlines fitted to the H:C and O:C versus mass loss data are shown with dotted lines. Uncertainty is presented for HP and BK wildfire chars as an average of the uncertainties for each char in those categories. Uncertainty is not shown for the engineered biochars due to negligible variability in mass loss and composition.

the data measured in this study and are included in Fig. 4. Biochar samples from Santín et al. (2017) include samples collected from the forest floor (FF) and downed wood (DW) before an experimental burn in a jack pine stand in boreal Canada, and then pyrolyzed at 350, 500, and 650 °C in the absence of O_2 for 2 h in the laboratory. FF samples, composed of needles, mosses, lichens, fermented litter and humidified organic material, and DW, consisting of dead down wood pieces of jack pine with diameters of 0.5–2 cm, underwent pyrolysis, and were then mixed and ground for ensuing proximate and elemental analysis. Wildfire chars from Santín et al. (2017) produced during the experimental fire were not used for comparison in Fig. 4 because the mass loss measurement method was not as rigorous as that used during biochar manufacture in the laboratory. Additionally, miscanthus, hops, mixed wood waste, and oak wood waste samples pyrolyzed at 300 °C in in a semi-inert atmosphere for 1.5 h in Ivanovski et al. (2021) are also shown in Fig. 4. Despite the variation in feedstocks and char formation conditions between Santín et al. (2017), Ivanovski et al. (2021), and this study, the trendlines fitted to the data in this study generally capture a correlation between increased mass loss and decreased H:C and O:C for the results from Santín et al. (2017) and Ivanovski et al. (2021) well. This result suggests applicability of the linear correlation results to a broad range of lignocellulosic fuels, but further testing and verification would be required to extend the use of these correlations to feedstocks other than the bark/cambium tested in this study.

3.3. Stable polycyclic aromatic carbon (SPAC) formation

The SPAC contents of wildfire chars and engineered biochars with respect to H:C molar ratios, O:C molar ratios, and mass loss are shown in Fig. 5. The SPAC contents of the limited O_2 engineered biochars were not analyzed in order to reduce the number of samples for the relatively cost- and effort-intensive HyPy procedure, and are not included in Fig. 5. SPAC contents are presented in units of wt% on a DAF char basis, and can also be interpreted as grams of SPAC formed per 100 g of char, also on a DAF basis. Linear correlations between SPAC content and molar H:C, molar O:C, and mass loss reveal dependence of SPAC formation on pyrolysis severity - with increased pyrolysis severity reflected as reduced H:C, reduced O:C, and increased mass loss - resulting from various combinations of gas environment temperature, pyrolysis duration, and gas environment. Linear trendlines were determined for chars with H:C and O:C molar values < 0.80 and 0.35 in Fig. 5a and b, respectively. A linear relationship between SPAC content and mass loss was determined for mass losses > 60 wt% in Fig. 5c. The linear trendlines for SPAC content with respect to molar H:C, molar O:C, and mass loss are provided in Eqs. (4), (5), and (6), respectively.

$$SPAC = -102 * H:C + 83.8. \quad (wt\%DAF,\ or\ \ gPyC\ per\ 100g\ DAF\ \ char) \tag{4}$$

$$SPAC = -192 * O:C + 66.4\ . \quad (wt\%DAF,\ or\ \ gPyC\ per\ 100g\ DAF\ \ char) \tag{5}$$

$$SPAC = 2.49 * Mass\ Loss\ (wt\%DAF) - 154. \quad (wt\%DAF,\ or\ \ gPyC\ per\ 100g\ DAF\ \ char) \tag{6}$$

R^2 values for Eqs. (4), (5), and (6) were found to be 0.67, 0.66, and 0.73, respectively.

Notably, the SPAC contents estimated using Eqs. (4)–(6) differed slightly using measured H:C, O:C, and mass loss for a given char, which is not unexpected considering the low linear regressions determined for the SPAC relationships. The SPAC contents of the limited O_2 biochars were predicted using Eqs. (4)–(6), and SPAC wt% for a given biochar varied by ±5 wt% across the three correlations. This result could be strengthened by including more HyPy-derived data in the derivations of Eqs. (4)–(6).

The SPAC measured in this work is the refractory aromatic content of chars that has the greatest environmental persistence, and is projected by current estimates to sequester carbon for > 1000 yrs (Santín et al., 2015; Haig et al., 2020; Spokas et al., 2012; Ascough et al., 2009; Rombolà et al., 2016; Rombolà et al., 2015; Meredith et al., 2012; Budai et al., 2013). The non-SPAC remainder of char is expected to degrade over shorter time periods after char deposition, such as in soil. The results of this study show that the H:C and O:C carbon longevity thresholds that have been identified for > 100 yrs. (H:C < 0.7 and O:C < 0.6) and > 1000 yr (O:C < 0.2) do not correspond to wildfire chars and engineered biochars composed entirely of SPAC. Chars with a molar H:C of 0.7 show a SPAC content of approximately 15 wt%, and chars with a molar O:C of 0.2 show a SPAC fraction of approximately 30 wt%. Notably, the results of this study also suggest a potential limit to SPAC formation of up to approximately 75 wt% of chars at high treatment severity. These magnitudes agree with

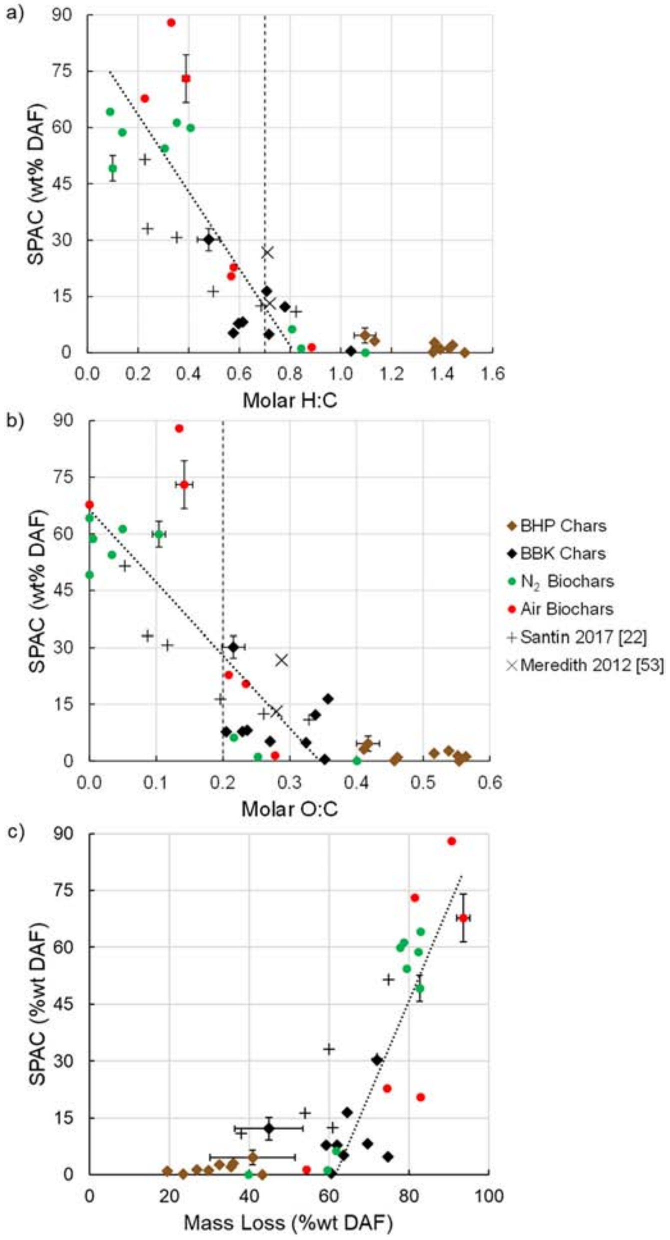

Fig. 5. SPAC content with respect to a) H:C, b) O:C, and c) mass loss on dry, ash-free (DAF) bases. Wildfire chars are grouped as burned healthy pine (BHP, brown diamond markers) and burned beetle-killed (BBK, black diamond markers), and laboratory-engineered biochars are grouped as N_2 (green round markers) and air (red round markers). SPAC and molar ratio data for feedstocks investigated by Santín et al. (2017) and Meredith et al. (2012) ((a) and (b) only) are included for comparison as "+" and "x" markers, respectively. The molar H:C value of 0.7 and O:C values of 0.6 and 0.2 that have been correlated with projected char carbon environmental persistence of > 100 and 1000 yr (Spokas et al., 2012; Budai et al., 2013) are identified using horizontal dashed lines. Linear trendlines fitted to the SPAC content versus H:C and O:C molar ratio and mass loss data are shown with dotted lines. Average uncertainties for each category of wildfire chars and engineered biochars – burned HP wildfire chars, burned BK wildfire chars, N_2 biochars, or air biochars – are shown.

the findings of Zimmerman (2010) and Rombolà et al. (2015) in which the C concentration of biochar-amended soils decreased 26–79 % over time in incubation studies performed using biochars manufactured at temperatures > 400 °C, and lower C loss corresponded to greater biochar pyrolysis severity.

Data from Santín et al. (2017) and Meredith et al. (2012) are included in Fig. 5 for different feedstocks treated in different environmental conditions. Data from Santín et al. (2017) include the SPAC contents of the FF and DW biochars described in Section 3.2, and the Q3 indices used in that study to quantify the thermally recalcitrant fractions of those biochars, identified using TGA and differential scanning calorimetry, were used as a proxy for HyPy-derived SPAC in this study. Meredith et al. (2012) reported C content of HyPy-treated biochars included in a 12-ring trial, where the HyPy method was evaluated for accuracy and robustness using the 12 reference materials from the International Black Carbon Ring Trial. Two of those reference samples included chestnut wood and grass biochars manufactured at 450 °C for 5 h under N_2. Data from Meredith et al. (2012) is not included in Fig. 5c because biochar mass loss was not reported in that study. Despite the differences in feedstocks and pyrolysis conditions between Santín et al. (2017), Meredith et al. (2012), and the present study, there is good agreement among the data in terms of the SPAC content in relation to H:C, O:C, and mass loss. As was noted in Section 3.2, these results suggest broad applicability of the models developed in this work, but these models will need to be tested and validated for other lignocellulose-derived wildfire chars and engineered biochars produced under a wide range of pyrolysis conditions, as was done in this study, before the models can be reliably applied more generally.

The SPAC data presented in this study showed relatively low levels of SPAC production in standing lodgepole pine fuels under MF wildfire conditions. HP wildfire chars showed SPAC contents of < 5 wt%, and most BK wildfire chars showed < 30 wt% SPAC content. These findings are consistent with recent studies indicating that many post-fire SPAC estimations have been overestimates (Santín et al., 2016; Howell et al., 2021). Notably, the MF was considered to be a relatively severe wildfire, occurring during a dry period in a forest highly impacted by the mountain bark beetle epidemic, in which at least 58 % of the forest basal area was standing dead fuel prior to the MF (Kayes and Tinker, 2012; Reed et al., 2014). Thus, while standing fuels can contribute to SPAC stores post-fire, engineered biochars have a greater potential to store highly environmentally stable PyC. Additionally, even biochars manufactured under the most severe pyrolysis conditions tested in this study, such as those produced at 800 °C in N_2 and air, are not composed entirely of SPAC and significant quantities of more labile PyC remain.

3.4. Carbon lost

The characterization methods utilized in this work can be applied to quantify the carbon lost during wildfire char or engineered biochar formation. The percentage of C that is lost during char formation as a function of mass loss is shown in Fig. 6a, and the corresponding quantities of SPAC formed are shown in Fig. 6b. Details of these calculations can be found in (Howell et al., 2021). The relationship between C loss and mass loss (Fig. 6a) is highly linear with a R^2 of 0.94 and is shown in Eq. 7

$$C\ Loss = 0.91 * Mass\ Loss\ (wt\%DAF) - 3.09. \tag{7}$$

Fig. 6b shows the gSPAC formed per 100 g of DAF raw biomass used to produce the wildfire chars and engineered biochars with respect to mass loss. SPAC contents of limited O_2 engineered biochars in Fig. 6b were determined using the average of SPAC contents predicted using Eqs. (4)–(6). Absolute quantities of SPAC formed per 100 g DAF raw biomass are relatively low – up to approximately 14 gSPAC for severely pyrolyzed biochars – due to high mass loss at these severe treatments. Notably, SPAC is consumed in the most severe oxidative pyrolysis conditions, which can be observed in a reduction of the gSPAC at the greatest char mass losses, as compared with the maximum gSPAC shown in Fig. 6b. Peak SPAC yields were obtained for engineered biochars with mass losses approximating the VC content of the raw biomass (~80 wt%), achieved in either inert or oxidative conditions, with higher mass losses yielding less SPAC due to oxidative losses.

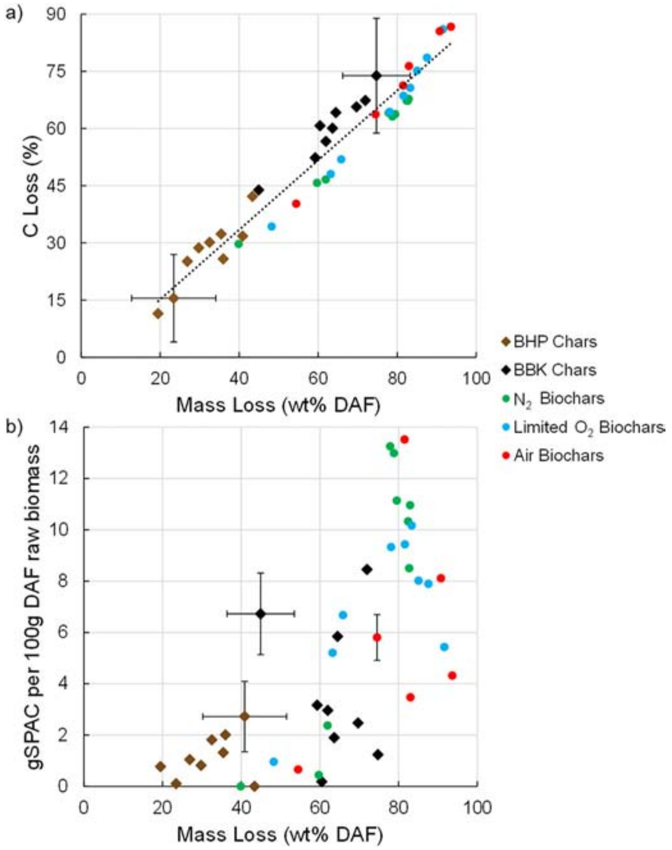

Fig. 6. a) Carbon loss and b) gSPAC formed per 100 g of dry, ash-free (DAF) raw biomass are shown with respect to DAF mass loss. Wildfire chars are grouped as burned healthy pine (BHP, brown diamond markers) and burned beetle-killed (BBK, black diamond markers), and laboratory-engineered chars are grouped as N_2 (green round markers), limited O_2 (blue round markers), and air (red round markers). Average uncertainty is presented for HP and BK chars. Average uncertainty of engineered biochars is shown for gSPAC formed, but not for C or mass loss due to negligible uncertainty values.

4. Conclusions

This study undertook a novel investigation into the relationships between pyrolysis mass loss, molar H:C and O:C, and SPAC content of wildfire chars and engineered biochars. The environmental conditions experienced by biomass during wildfires is a major gap in current research knowledge and presents challenges for developing models of the carbon released and retained after fire events for global carbon accounting. Additionally, accurate knowledge of the environmental stability of engineered biochars is needed to predict the effectiveness of these biochars for CDR. Robust characterization and modeling of the oxidative pyrolysis conditions experienced during wildfire and often utilized for producing engineered biochars is challenging for a variety of reasons, and presents limitations for reliably characterizing char stability for carbon sequestration models.

The correlations between mass loss and H:C and O:C molar ratios identified in this study show that precise knowledge of the formation conditions during wildfires or engineered biochar production is not needed to relate physicochemical char properties as they change with pyrolysis severity. Additionally, results show that engineered biochars can be compared to wildfire-generated chars despite the differences in wildfire and engineered formation. Only two fuels – healthy and beetle-killed bark/cambium – were characterized in this study, but the correlations determined for these fuels were found to accurately represent a range of lignocellulosic feedstocks, suggesting broader applicability of the results for both wildfire chars and engineered biochars.

Similarly linear correlations between SPAC content and molar H:C, molar O:C, and mass loss of wildfire chars and engineered biochars were shown. The SPAC models developed in this work can be used to quantify carbon fluxes and carbon reservoirs in wildfire chars and engineered biochars without the need for full-scale field studies or specialized SPAC characterization methods such as the hydrogen pyrolysis procedure used in this work. Finally, an assessment of the dependence of carbon loss and SPAC yields on overall pyrolysis severity was made. Results show that increased severity leads to greater absolute SPAC formation, despite a concomitant increase in carbon loss, though the most severe oxidative pyrolysis conditions did result in SPAC consumption. The findings of this work can significantly improve SPAC assessments for global carbon accounting. Furthermore, the methodology developed in this work can be readily applied to other significant SPAC sources such as down wood and forest floor fuels from wildfires and engineered biochars produced from other feedstocks.

Credit authorship contribution statement

Alexandra Howell: Conceptualization, Design, Methodology, Experimentation, Data analysis, Writing.

Sophia Helmkamp: Experimentation, Data analysis.

Dr. Erica Belmont: Conceptualization, Design, Methodology, Data analysis, Writing, Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

The authors own a business focused on CDR, including biochar-based CDR.

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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.2022.157610.

References

Ascough, P.L., et al., 2009. Hydropyrolysis as a new tool for radiocarbon pre-treatment and the quantification of black carbon. Quat. Geochronol. 4, 140–147.

Ascough, D.C., Bird, P.L., Meredith, M.I., Wood, W., Snape, R.E., Brock, C.E., Higham, F., Large, T.F.G., Apperley, D.J., 2010. Hydropyrolysis: implications for radiocarbon pretreatment and characterization of black carbon. Radiocarbon 52 (2), 1336–1350.

Ascough, P.L., et al., 2010. Charcoal reflectance measurements: implications for structural characterization and assessment of diagenetic alteration. J. Archaeol. Sci. 37 (7), 1590–1599.

Ascough, P.L., et al., 2011. Variability in oxidative degradation of charcoal: influence of production conditions and environmental exposure. Geochim. Cosmochim. Acta 75 (9), 2361–2378.

Ascough, P.L., Bird, M.I., Meredith, W., Snape, C.E., 2016. Dates and fates of pyrogenic carbon: using spectroscopy to understand a 'missing' global carbon sink. Spectrosc. Eur. 28 (2), 6–9.

Ascough, P.L., Brock, F., Collinson, M.E., Painter, J.D., Lane, D.W., Bird, M.I., 2020. Chemical characteristics of macroscopic pyrogenic carbon following millennial-scale environmental exposure. Front. Environ. Sci. 7 (January), 1–15.

ASTM, 2013. Standard practice for ultimate analysis of coal and coke. Annu. B. ASTM Stand. 60, 3174–3175.

Belcher, C.M., Hudspith, V.A., 2016. The formation of charcoal reflectance and its potential use in post-fire assessments. Int. J. Wildl. Fire 25 (7), 775–779.

Belcher, C.M., et al., 2018. What can charcoal reflectance tell us about energy release in wildfires and the properties of pyrogenic carbon? Front. Earth Sci. 6 (October), 1–13.

Berner, J.A., Logan, T., Law, Law, Beverly E., Meddens, Arjan J.H., Hicke, 2012. Tree mortality from fires, bark beetles, and timber harvest during a hot and dry decade in the western United States (2003-2012). Environ. Res. Lett. 12 (6).

Bird, M.I., Wynn, J.G., Saiz, G., Wurster, C.M., McBeath, A., 2015. The pyrogenic carbon cycle. Annu. Rev. Earth Planet. Sci. 43, 273–298.

Bis, Z., Kobyłecki, R., Ścisłowska, M., Zarzycki, R., 2018. Biochar – potential tool to combat climate change and drought. Ecohydrol. Hydrobiol. 18 (4), 441–453.

Bruun, S., Jensen, E.S., Jensen, L.S., 2008. Microbial mineralization and assimilation of black carbon: dependency on degree of thermal alteration. Org. Geochem. 39 (7), 839–845.

Budai, A., et al., 2013. Biochar carbon stability test method : an assessment of methods to determine biochar carbon stability. Int. Biochar Initiat. 1–10.

Cao, X., et al., 2012. Characterization of wood chars produced at different temperatures using advanced solid-state 13C NMR spectroscopic techniques. Energy Fuel 26 (9), 5983–5991.

Chen, J., et al., 2021. The comparison study of multiple biochar stability assessment methods. J. Anal. Appl. Pyrolysis 156 (January), 105070.

Cheng, C.H., Lehmann, J., Thies, J.E., Burton, S.D., Engelhard, M.H., 2006. Oxidation of black carbon by biotic and abiotic processes. Org. Geochem. 37 (11), 1477–1488.

Cotrufo, M.F., et al., 2016. Quantification of pyrogenic carbon in the environment: an integration of analytical approaches. Org. Geochem. 100, 42–50.

Doerr, S.H., Santín, C., Merino, A., Belcher, C.M., Baxter, G., 2018. Fire as a removal mechanism of pyrogenic carbon from the environment: effects of fire and pyrogenic carbon characteristics. Front. Earth Sci. 6 (October), 1–13.

Glaser, B., Guggenberger, G., Zech, W., 2001. Black carbon in sustainable soils of the Brazilian Amazon region. Underst. Manag. Org. Matter Soils, Sediments Waters 31 (January 2001), 359–364.

Guizani, C., Jeguirim, M., Valin, S., Peyrot, M., Salvador, S., 2019. The Heat Treatment Severity Index: a new metric correlated to the properties of biochars obtained from entrained flow pyrolysis of biomass. Fuel 244 (June 2018), 61–68.

Hagemann, N., Spokas, K., Schmidt, H.P., Kägi, R., Böhler, M.A., Bucheli, T.D., 2018. Activated carbon, biochar and charcoal: linkages and synergies across pyrogenic carbon's ABCs. Water (Switzerland) 10 (2), 1–19.

Haig, J., Bird, M.I., Ascough, P.L., Wurster, C.M., 2020. A rapid throughput technique to isolate pyrogenic carbon by hydrogen pyrolysis for stable isotope and radiocarbon analysis. Rapid Commun. Mass Spectrom. 34, 1–11.

Hammes, K., et al., 2007. Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. Glob. Biogeochem. Cycles 21.

Harvey, B.J., Donato, D.C., Turner, M.G., 2014. Recent mountain pine beetle outbreaks, wildfire severity, and postfire tree regeneration in the US Northern Rockies. Proc. Natl. Acad. Sci. 111 (42).

Hindasageri, V., Vedula, R.P., Prabhu, S.V., 2013. Thermocouple error correction for measuring the flame temperature with determination of emissivity and heat transfer coefficient. Rev. Sci. Instrum. 84 (2).

Howell, A., Bretfeld, M., Belmont, E., 2021. Impacts of bark beetle-induced tree mortality on pyrogenic carbon production and heat output in wildfires for fire modeling and global carbon accounting. Sci. Total Environ. 760, 144149.

Ivanovski, M., Goricanec, D., Krope, J., Urbancl, D., 2021. Torrefaction pretreatment of lignocellulosic biomass for sustainable solid biofuel production. Energy (xxxx), 122483.

Jones, M.W., Santín, C., Van Der Werf, G.R., Doerr, S.H., 2019. Global fire emissions buffered by the production of of pyrogenic carbon. Nat. Geosci. 12 (September), 742–747.

Joseph, S., et al., 2021. How biochar works, and when it doesn't: a review of mechanisms controlling soil and plant responses to biochar. GCB Bioenergy (January), 1–34.

Kayes, L.J., Tinker, D.B., 2012. Forest structure and regeneration following a mountain pine beetle epidemic in southeastern Wyoming. For. Ecol. Manag. 263, 57–66.

Koele, N., et al., 2017. Amazon Basin forest pyrogenic carbon stocks: first estimate of deep storage. Geoderma 306 (August), 237–243.

L. Krotz, F. Leone, and G. Giazzi, "Thermo Scientific Flash Smart Elemental Analyzer: Fully Automated Double Channel Analysis for Petrochemical Applications.

Kuzyakov, Y., Bogomolova, I., Glaser, B., 2014. Biochar stability in soil: decomposition during eight years and transformation as assessed by compound-specific 14C analysis. Soil Biol. Biochem. 70, 229–236.

Landry, J.S., Matthews, H.D., 2017. The global pyrogenic carbon cycle and its impact on the level of atmospheric CO2 over past and future centuries. Glob. Chang. Biol. 23 (8), 3205–3218.

Leng, L., Huang, H., 2018. An overview of the effect of pyrolysis process parameters on biochar stability. Bioresour. Technol. 270 (August), 627–642.

Leng, L., Huang, H., Li, H., Li, J., Zhou, W., 2019. Biochar stability assessment methods: a review. Sci. Total Environ. 647, 210–222.

Lian, F., Xing, B., 2017. Black carbon (Biochar) in Water/Soil environments: molecular structure, sorption, stability, and potential risk. Environ. Sci. Technol. 51 (23), 13517–13532.

Matosziuk, L.M., Alleau, Y., Kerns, B.K., Bailey, J., Johnson, M.G., Hatten, J.A., 2019. Effects of season and interval of prescribed burns on pyrogenic carbon in ponderosa pine stands in the southern Blue Mountains, Oregon, USA. Geoderma 348 (December 2018), 1–11.

McBeath, A.V., Smernik, R.J., Krull, E.S., 2013. A demonstration of the high variability of chars produced from wood in bushfires. Org. Geochem. 55, 38–44.

McBeath, A.V., Wurster, C.M., Bird, M.I., 2015. Influence of feedstock properties and pyrolysis conditions on biochar carbon stability as determined by hydrogen pyrolysis. Biomass Bioenergy 73, 155–173.

McParland, L.C., Collinson, M.E., Scott, A.C., Campbell, G., 2009. The use of reflectance values for the interpretation of natural and anthropogenic charcoal assemblages. Archaeol. Anthropol. Sci. 1 (4), 249–261.

Meredith, W., et al., 2012. Assessment of hydropyrolysis as a method for the quantification of black carbon using standard reference materials. Geochim. Cosmochim. Acta 97, 131–147.

Minx, J.C., 2018. Negative emissions - Part 1: research landscape and synthesis. Environ. Res. Lett. 13 (6).

"Mullen Fire," incident information system. [Online]. Available: https://inciweb.nwcg.gov/incident/7208/.

Preston, C.M., Schmidt, M.W.I., 2006. Black (pyrogenic) carbon : a synthesis of current knowledge and uncertainties with special consideration of boreal regions. Biogeosciences 3, 397–420.

W. S. Rasband, "ImageJ," Bethesda, Maryland, USA.

Reed, D.E., Ewers, B.E., Pendall, E., 2014. Impact of mountain pine beetle induced mortality on forest carbon and water fluxes. Environ. Res. Lett. 9.

Rombolà, A.G., et al., 2015. Fate of soil organic carbon and polycyclic aromatic hydrocarbons in a vineyard soil treated with biochar. Environ. Sci. Technol. 49 (18), 11037–11044.

Rombolà, A.G., Fabbri, D., Meredith, W., Snape, C.E., Dieguez-Alonso, A., 2016. Molecular characterization of the thermally labile fraction of biochar by hydropyrolysis and pyrolysis-GC/MS. J. Anal. Appl. Pyrolysis 121, 230–239.

Santín, C., Doerr, S.H., Preston, C., Bryant, R., 2013. Consumption of residual pyrogenic carbon by wildfire. Int. J. Wildl. Fire 22 (8), 1072–1077.

Santín, C., Doerr, S.H., Preston, C.M., González-Rodríguez, G., 2015. Pyrogenic organic matter production from wildfires: a missing sink in the global carbon cycle. Glob. Chang. Biol. 21 (4), 1621–1633.

Santín, C., et al., 2016. Towards a global assessment of pyrogenic carbon from vegetation fires. Glob. Chang. Biol. 22 (1), 76–91.

Santín, C., et al., 2017. Carbon sequestration potential and physicochemical properties differ between wildfire charcoals and slow-pyrolysis biochars. Sci. Rep. 7 (1), 1–11.

Santin, C., Doerr, S.H., Jones, M.W., Merino, A., Warneke, C., Roberts, J.M., 2020. The relevance of pyrogenic carbon for carbon budgets from fires: insights from the FIREX experiment. Glob. Biogeochem. Cycles 34 (9), 1–17.

Schneider, M.P.W., Hilf, M., Vogt, U.F., Schmidt, M.W.I., 2010. The benzene polycarboxylic acid (BPCA) pattern of wood pyrolyzed between 200°C and 1000°C. Org. Geochem. 41 (10), 1082–1088.

Schneider, M.P.W., Pyle, L.A., Clark, K.L., Hockaday, W.C., Masiello, C.A., Schmidt, M.W.I., 2013. Toward a 'molecular thermometer' to estimate the charring temperature of wildland charcoals derived from different biomass sources. Environ. Sci. Technol. 47 (20), 11490–11495.

Shannon, K.S., Butler, B.W., 2003. A review of error associated with thermocouple temperature measurement in fire environments. Int. Wildland Fire Ecol. (August 2015), 7–9.

Soucémarianadin, L.N., Quideau, S.A., MacKenzie, M.D., Bernard, G.M., Wasylishen, R.E., 2013. Laboratory charring conditions affect black carbon properties: a case study from Quebec black spruce forests. Org. Geochem. 62, 46–55.

Spokas, K.A., 2010. Review of the stability of biochar in soils: predictability of O: C molar ratios. Carbon Manag. 1 (2), 289–303.

Spokas, K.A., et al., 2012. Biochar: a synthesis of its agronomic impact beyond carbon sequestration. J. Environ. Qual. 41 (4), 973–989.

Surawski, N.C., Sullivan, A.L., Roxburgh, S.H., Meyer, C.P.M., Polglase, P.J., 2016. Incorrect interpretation of carbon mass balance biases global vegetation fire emission estimates. Nat. Commun. 7 (May), 1–5.

Weber, K., Quicker, P., 2018. Properties of biochar. Fuel 217 (September 2017), 240–261.

Weng, Z., et al., 2017. Biochar built soil carbon over a decade by stabilizing rhizodeposits. Nat. Clim. Chang. 7 (5), 371–376.

Wurster, C.M., Saiz, G., Schneider, M.P.W., Schmidt, M.W.I., Bird, M.I., 2013. Quantifying pyrogenic carbon from thermosequences of wood and grass using hydrogen pyrolysis. Org. Geochem. 62, 28–32.

Zimmerman, A.R., 2010. Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). Environ. Sci. Technol. 44 (4), 1295–1301.

Zimmerman, A.R., Mitra, S., 2017. Trial by fire: on the terminology and methods used in pyrogenic organic carbon research. Front. Earth Sci. 5 (November).