

## Fuel moisture influences on fire-altered carbon in masticated fuels: An experimental study

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[1] Biomass burning is a significant contributor to atmospheric carbon emissions but may also provide an avenue in which fire-affected ecosystems can accumulate carbon over time, through the generation of highly resistant fire-altered carbon. Identifying how fuel moisture, and subsequent changes in the fire behavior, relates to the production of fire-altered carbon is important in determining how persistent charred residues are following a fire within specific fuel types. Additionally, understanding how mastication (mechanical forest thinning) and fire convert biomass to black carbon is essential for understanding how this management technique, employed in many fire-prone forest types, may influence stand-level black carbon in soils. In this experimental study, 15 masticated fuel beds, conditioned to three fuel moisture ranges, were burned, and production rates of pyrogenic carbon and soot-based black carbon were evaluated. Pyrogenic carbon was determined through elemental analysis of the post-fire residues, and soot-based black carbon was quantified with thermochemical methods. Pyrogenic carbon production rates ranged from 7.23% to 8.67% relative to pre-fire organic carbon content. Black carbon production rates averaged 0.02% in the 4–8% fuel moisture group and 0.05% in the 13–18% moisture group. A comparison of the ratio of black carbon to pyrogenic carbon indicates that burning with fuels ranging from 13% to 15% moisture content resulted in a higher proportion of black carbon produced, suggesting that the precursors to black carbon were indiscriminately consumed at lower fuel moistures. This research highlights the importance of fuel moisture and its role in dictating both the quantity and quality of the carbon produced in masticated fuel beds.

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### 1. Introduction

[2] Forested terrestrial ecosystems have recently received attention for their potential role in sequestering carbon (C) to help offset global greenhouse gas emissions from fossil fuel and biomass burning [Pacala and Socolow, 2004; Pan *et al.*, 2011]. As a result of this attention, policy and management efforts are currently being encouraged to account for carbon at the stand level [Canadell and Raupach, 2008]. Carbon cycling in fire-prone forests is inherently complex because of numerous factors acting on the stand

over time [McKinley *et al.*, 2011]. In a given forest, biomass accumulation periods (C sink as aboveground carbon pools grow) are often followed by a disturbance processes, e.g., land conversion, harvesting, fire, insects, and wind. These disturbances can rapidly deplete existing carbon and transition biomass from live to dead pools, where slow decomposition continues to release carbon into the atmosphere [McKinley *et al.*, 2011]. Given enough time, the stand may successfully regain its pre-disturbance carbon stocks, and when considered over broad temporal and spatial scales, this gain/loss carbon cycling may reach equilibrium [Harmon, 2001; Kashian *et al.*, 2006]. A potential key contributor to long-term carbon storage in fire-affected ecosystems is the production of fire-altered charred residues [Goldberg, 1985]. This thermally altered biomass has the potential to persist in terrestrial soils for thousands of years, thereby slowly increasing forest soil carbon stocks over multiple fire events [DeLuca and Aplet, 2008].

[3] Pyrogenic carbon (pyrC) in fire-altered residues exists on a continuum, ranging from partially charred plant material to black carbon (BC) and re-condensed soot, and fire temperature is the primary variable determining the chemical

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characteristics associated with the charred residues [Keiluweit *et al.*, 2010; Masiello, 2004; Preston and Schmidt, 2006]. Partially charred vegetation is typically associated with low formation temperatures (100–500 °C), whereas soot and BC form under high-temperature combustion conditions (700–1000 °C) [Keiluweit *et al.*, 2010; Schmidt and Noack, 2000]. The ultimate end of the continuum is incombustible mineral ash, which results from the complete combustion of the charred residues [Smith and Hudak, 2005; Smith *et al.*, 2005]. In the present study, the term “charred residues” or “post-fire residues” refers to the entire mass of material following combustion, including ash. Because of differences in fire-altered carbon quantification procedures and terminology used, the present study will differentiate between “pyrogenic carbon” and “black carbon,” in an attempt to maintain consistent definitions presented in Preston and Schmidt [2006]. The term “pyrogenically altered carbon” will encompass the entire spectrum of fire-affected carbon, from partially altered residues to ash and soot. Inherent within this spectrum are residues that have been thermally altered but may not be blackened on the surface or entirely blackened throughout the cores of larger charred particles. Visual separation is an insufficient method to differentiate unaltered material from particles that have been subjected only to the initial stages of thermal alteration. Therefore, pyrC in this study includes all thermally altered residues of the remaining biomass because it was all subjected to at least some degree of heating via flaming and smoldering combustion. Soot-based black carbon (soot-BC) specifically captures the highly resistant portion of the pyrC spectrum and will be quantified through adapted CTO-375 methods, commonly used to measure soot-BC in ocean sediments [Sánchez-García *et al.*, 2012]. Although this method detects primarily diesel soot, it also likely captures BC formed from biomass burning at high (700–1000 °C) combustion temperatures [Elmquist *et al.*, 2006]. As a result of its highly thermally altered chemical structure, soot-BC may reside in soils and sediments for decadal to millennial time scales [Schmidt *et al.*, 2011].

[4] Fuel characteristics and the resulting subsequent combustion environment ultimately control the production of pyrC in wildland fuels [Czimczik and Masiello, 2007]. During combustion, both aromatic (e.g., lignin) and non-aromatic (e.g., cellulose) compounds contribute to the formation of pyrC [Shafizadeh, 1984]. Fuel types with high lignin-to-cellulose ratios (e.g., forests) produce large amounts of BC relative to cellulose-dominated fuel types, probably as a result of the precursors having chemical characteristics similar to those of the pyrC [Czimczik *et al.*, 2005]. Production of pyrC and soot-BC is also a likely function of the fire behavior within specific fuel types, in which the degree of thermal alteration to the chemical structure is dependent primarily on fire temperature as well as heating duration [Keiluweit *et al.*, 2010]. Despite the relative importance of fuel properties (e.g., fuel arrangement and moisture) on fire behavior, very few studies that attempt to characterize the differences in pyrC and within specific wildland fuel types are available [Alexis *et al.*, 2007; Eckmeier *et al.*, 2007; Fearnside *et al.*, 2001], and to our knowledge, soot-BC production from biomass burning has not yet been evaluated. However, studies of charring intensity in oxygen-poor isothermal conditions (e.g., a muffle furnace) found that BC production is higher in

high-temperature as opposed to low-temperature conditions [Keiluweit *et al.*, 2010], suggesting that within specific fuel types charcoal production is likely highly variable because of the dynamic nature of the fire behavior, even within specific fuel types at the stand level.

[5] Fire intensity in wildland settings is broadly linked to fuels, weather, and topography [Pyne *et al.*, 1996], with weather being the most dynamic variable, not only influencing the moisture of the fuels on a seasonal and daily basis but also affecting the ambient temperature, relative humidity, and wind speed of the immediate fire environment [Bessie and Johnson, 1995]. In temperate forest types of the western United States, fuel moisture is often a key variable determining fire behavior, fire severity, and surface biomass consumption within specific fuel types [Alexander, 1982; Anderson *et al.*, 2010; Brown *et al.*, 1991; Little *et al.*, 1986; Reinhardt *et al.*, 1991]. Increased fuel moisture decreases overall heat yield as a result of the increased energy requirements to raise a particle to ignition temperature [Van Wagner 1972]. Given the relationship between fuel moisture and fire behavior, we hypothesize that the moisture of the fuel will also be critical in determining the amount of charred residue remaining, as well as pyrC and soot-BC production in masticated fuel beds. Linking pre-fire fuel moisture to the fire’s behavior and subsequent pyrC and soot-BC production will provide indirect evidence of the importance of fuel moisture in controlling the production of fire-altered carbon.

[6] Throughout many forests of the western United States, successful fire exclusion policies have led to large increases in biomass accumulation [Moore *et al.*, 2004], leading to the increased use of thinning and prescribed fires to reduce excessive build-up of fuels [Agee and Skinner, 2005]. These management practices remove aboveground carbon to increase stand resilience to future disturbance, which is increasingly important in the face of climate change and increasing fire frequencies [Mitchell *et al.*, 2009; Westerling *et al.*, 2006]. Mastication is an increasingly utilized forest-thinning treatment in which equipment is used to grind down smaller trees and shrubs, effectively reallocating aerial fuels to the forest floor [Battaglia *et al.*, 2010]. Oftentimes prescribed fire treatment follows mastication to reduce surface fuel loadings and to further reduce the threat of high-intensity wildfires [Agee and Skinner, 2005].

[7] The implications of these management activities on carbon stocks vary widely by ecosystem type [McKinley *et al.*, 2011; Mitchell *et al.*, 2009]. Although fuels reduction activities may temporarily reduce stand-level carbon stocks, thinning smaller-diameter trees may actually increase stand-level carbon over time, given that large-diameter trees store a disproportionately greater amount of aboveground carbon [Hurteau and Brooks, 2011]. However, at the landscape level, it is expected that forest carbon will generally decline through thinning and burning [McKinley *et al.*, 2011; Reinhardt and Holsinger, 2010]. The contribution of fire-altered carbon produced during prescribed fires has yet to be effectively incorporated in stand-level carbon budgets, yet this may contribute to a slowly growing passive carbon pool in forest soils through the repeated application of prescribed burning and wildfire [DeLuca and Aplet, 2008; Hurteau and North, 2009]. Research examining effects of fuels treatments on C storage would benefit greatly from the inclusion of pyrC and soot-BC production for their post-fire C budgets [Hurteau and Brooks, 2011].

[8] In response to these needs, we designed an experiment to evaluate the role of fuel moisture on the production of charred residues, pyrC, and soot-BC in masticated fuels using a representative masticated fuel bed from a mixed conifer stand, commonly found throughout the interior western United States. We conditioned 15 experimentally created masticated fuel beds to three predefined moisture groups (4–8%, 10–12%, and 13–16%), burned them, and measured the remains. The objectives of this study were to (1) identify changes in fire behavior characteristics in the masticated fuel beds as a function of fuel moisture, (2) quantify the pyrC and soot-BC in masticated fuels under the three preset fuel moisture levels, and (3) evaluate the relative degree of resistance to biologic degradation of the fire-altered carbon produced from burning at the three moisture levels by comparing the ratio of soot-BC to overall pyrC production.

## 2. Methods

### 2.1. Fuel Bed Construction

[9] An 8 ha mixed conifer stand comprising white pine (*Pinus monticola*) and Douglas fir (*Pseudotsuga menziesii*) ingrown with lodgepole pine (*Pinus contorta*) in the Clearwater National Forest (latitude 46.801 N, longitude 119.47 W) in Idaho was masticated in June 2009. Mastication thinning was implemented in the stand to reduce canopy bulk density and wildfire risk as well as to improve stand health for the remaining trees. Masticated particles were primarily chipped into smaller-diameter (<7.6 cm) particles, although large-diameter >7.6 cm particles were also present. Fuel loading from this stand was established to ensure that our laboratory-created fuel beds closely resembled conditions in the field. The stand was sampled for fuel loading using square frame methods adapted from *Hood and Wu* [2006]. From a random start location within the stand, a quadrat (0.37 m<sup>2</sup>) was placed at distances of 5, 10, 15, 20, and 25 m from the starting point in the four cardinal directions for a total of 20 plots. Fuel bed height measurements were taken at the four corners of the quadrat and once in the center, and fuel bed bulk density was determined by dividing the dry weight of fuel within the quadrat by the volume of the fuel bed. Fuels within the quadrat were removed to mineral soil, placed in a bag, and transported back to the University of Idaho’s Fire Laboratory. Because of their high degree of spatial variability, fuels >7.6 cm in diameter were excluded from the experiment. Fuels from each of the 20 plots were then individually sorted into five different size classes (7.6–2.5 cm, 2.5–1.3 cm, 1.3–0.6 cm, 0.6–0.3 cm, and litter), dried at 100 °C until weights remained constant, and weighed. Fuel loadings for these fuel beds averaged 58.35 Mg ha<sup>-1</sup>, which were slightly lower than masticated fuel loadings in mixed conifer stands measured in Colorado [Battaglia et al., 2010].

[10] In addition to samples taken for fuel loading determination, masticated fuels were collected en masse from the site and also sorted in a similar manner for construction of the experimental fuel beds. Fifteen fuel beds were then assembled by recombining the sorted particles, using estimates of average dry weights of each size class. Replicates of five fuel beds were randomly assigned to one of three predetermined moisture levels of 4–8%, 10–12%, and 13–16%; fuel moisture was measured as a proportion of the dry weight.

[11] The pre-constructed fuel beds were stored in a chamber in which average fuel moistures ranged from 10% to 12%. The five fuel beds to be dried to 3–8% were taken from the control chamber on the day of the burn trial and were dried in a convection oven for 4 h at 37.5 °C to simulate temperature conditions similar to those of a hot summer day in the northern Rocky Mountains when a wildfire might occur. The five fuel beds to be burned at the 13–16% level were exposed to ambient conditions during the spring months of March and April to simulate conditions that might exist during prescribed fire settings. Prior to ignition for each burn, fuel moisture samples were taken from a small bin of excess fuel particles allowed to condition similarly to the fuel beds ( $n = 10$  for each size class of the fuel bed). Fuel moisture was calculated as a percentage of the dry weight. Fuel bed bulk densities averaged 102.05 g<sup>-2</sup> ( $n = 15$ ). Ambient air temperature in the burn chamber was 21.15 °C, and relative humidity averaged 35.07% ( $n = 15$ ).

[12] Pre-fire samples of masticated wood particles and pine needles were elementally analyzed for organic carbon (OC) content. The samples were milled in a grinder, dry sieved through a 500 µm mesh screen, and analyzed for C and N via methods described below. Pre-fire OC content for the organic matter was calculated by multiplying the % OC data for the needles and wood by the mass of the fuel bed. This study included only surface organic matter and not the mineral soil horizon because we did not wish to contaminate our samples with mineral soil.

### 2.2. Active Fire Measurements

[13] After proper moisture conditioning, the individual fuel beds were thoroughly mixed in a large bin for 1 min, spread onto the burn platform over the 0.37 m<sup>2</sup> area, and compressed by hand to achieve bulk densities similar to those observed in the field. These methods provided an accurate portrayal of the fuels given the highly disorganized nature of masticated fuel beds observed in the field. To address any potential “edge effects” on fire behavior, we extended a 20 cm buffer of additional masticated fuel 20 cm beyond the edge of the burn platform in all directions. Temperature and relative humidity readings were recorded every 5 min throughout the trial with a Kestrel® 3000 pocket weather meter to validate that ambient conditions were not responsible for differences in fire behavior (Table 1).

**Table 1.** Mean (SD) Fire Characteristics for Each Fuel Moisture Category<sup>a</sup>

Moisture Group	Flame Height (cm)	Flame Time (min:s)	Smolder Time (h:min:s)
4–8%	30.00 (6.00) a	18:45 (4:16) a	2:40:02 (1:06:53)
10–12%	23.00 (4.00) a	28:00 (9:34) a	2:11:04 (1:31:14)
13–16%	12.00 (4.00) b	45:36 (11:36) b	3:03:00 (46:38)
<i>p</i> -value	0.001	0.001	0.525

<sup>a</sup>*p*-values for ANOVA results between moisture levels. Homogenous subsets from Tukey’s post hoc analysis identified by a, b, and c ( $\alpha = 0.05$ ).  $n = 5$  for each moisture group.

The fuel beds were burned on a Sartorius EB Series scale (Goettingen, Germany). To minimize the effects of unwanted conductive heat transfer through the surface of the scale, we placed a  $0.37\text{ m}^{-2}$  3000 °F Ceramic Board (Cotronics Corp., Brooklyn, NY) over the scale. For ignition, a small amount of lighter fluid was added to a strip of buffer material surrounding the area of observation, which was then ignited and allowed to carry the flame across the burn platform. Two video cameras were used to record flame height and flaming time through the duration of the burn, one perpendicular to the ignition strip and the other in line with the flame front. Two 1.5 m incremented rulers were placed in view of the cameras, and flame heights were measured every 30 s throughout flaming combustion. Flaming time was measured beginning when flames reached the burn platform and extending until no visible flames remained on the platform. Smoldering combustion time was measured from the time when flaming ceased until mass was no longer lost. The burn trial was considered complete once mass loss ceased.

### 2.3. Post-fire Residue Analysis

[14] Several measurements were used to characterize the post-fire residues. All measurements were made within the  $0.37\text{ m}^2$  area and not from edge buffer material surrounding the burn platform. Residue mass was first established by weighing post-fire materials immediately following the burn trial, and consumption was measured by subtracting the post-fire residues, including ash content, from the pre-fire biomass dry weight. Charred residue production was then calculated by dividing the residue mass by the pre-fire dry weight. The residue mass also included partially charred materials and particles with charred rinds surrounding visibly uncharred cores, although their contribution to the total mass was negligible (less than 3%). Residues were then dry sieved into three size classes (<1 mm, 1–6 mm, and >6 mm) and weighed, given that the composition of each size class was likely to vary as a function of parent materials [Nocentini et al., 2010]. Size classes were chosen based on easily distinguishable characteristics. The charred >6 mm residues were produced from woody fuels, the 1–6 mm residues were primarily burned pine needles, and <1 mm residues consisted of ash and soot.

[15] Two samples from each fuel bed were then taken from each size class for further analysis, one for pyrC and the other for soot-BC analysis. Ash content was not removed for the pyrC calculations. Concentrations of post-fire pyrC and nitrogen (N) in all samples were measured via high temperature combustion (ECS 4010; Costech Analytical, Valencia, CA). Carbon to nitrogen (C:N) ratios were calculated by molar ratio. To gain insight into the mechanisms of OM alteration during burning, we analyzed the stable carbon isotopic composition of the unburned, burned, and soot-BC materials. This allowed us to determine whether isotopically distinct compounds (e.g., lignin is lighter than cellulose) were asymmetrically affected by burning [Bird and Ascough, 2012]. The stable isotopic compositions of OC ( $\delta^{13}\text{C}$ ) were determined on samples using high temperature combustion coupled with isotope ratio mass spectrometry (Delta Plus XP; Thermofinnigan, Bremen, Germany) [Brenna et al., 1997; Qi et al., 2003]. Isotopic reference materials were interspersed with samples for calibration. Contribution of  $\text{O}^{17}$  was corrected in IRMS software using

the Santrock correction [Santrock et al., 1985]. PyrC concentration (%C) was multiplied by the mass ( $\text{g m}^{-2}$ ) of the post-fire residue to calculate pyrC production for each of the fuel beds ( $\text{g m}^{-2}$ ).

[16] The second sample was analyzed for soot-BC using an adapted two-step thermochemical method described in Gustafsson et al. [1997] and Hatten and Zabowski [2009]. Samples were dried at 100 °C, weighed, spread evenly across the bottom of a 35 mm ceramic crucible, and placed in a preheated muffle furnace at 375 °C for 20 h to remove any organic, non-recalcitrant carbon. Care was taken to maintain a sample thickness of <1 mm to prevent additional pyrolysis from occurring in the muffle furnace. Samples were then treated with 6N HCl to remove any carbonates that might remain in the sample. After the thermochemical treatment, the samples were elementally analyzed, using the same methods as described above for pyrC, soot-BC, and soot-based black nitrogen (soot-BN) concentrations (%), and  $\delta^{13}\text{C}$  isotope determination. Soot-BC and soot-BN production ( $\text{g m}^{-2}$ ) was then calculated by multiplying the proportion of the sample resistant to thermal oxidation by the proportion resistant to chemical oxidation, then by the mass of the charred post-fire residue. Masses of the pyrC and soot-BC were also normalized by pre-fire OC content to determine pyrC and soot-BC production rates. The ratio of soot-BC to pyrC then provided a proxy for determining the relative biologic recalcitrance of the post-fire carbon [Hatten and Zabowski, 2009].

### 2.4. Statistical Analysis

[17] One-way analysis of variance (ANOVA) with Tukey post hoc analysis was used to test for differences across the three moisture groups for (1) post-fire residue mass, (2) pyrogenic and soot-BC concentrations, (3) pyrC production, (4) soot-BC production, (5) the soot-BC:pyrC ratio, (6) pyrC and soot-BC isotopes, and (7) pyrC:N and soot-BC:BN ratios. All statistical analysis was conducted with IBM SPSS predictive analytics software, version 19.

## 3. Results and Discussion

### 3.1. Fire Characteristics

[18] Regardless of fuel moisture, the flames initially spread across the table, burning primarily the top layer of masticated fuels and needles, and then continued to burn downward into the fuel bed. Visible charring of the residues on the burn platform was approximately 97–100%, given that the continuous nature of the masticated fuels allowed for sustained flaming combustion across the entire fuel bed. Following the initial flame front, fuel bed combustion continued in both flaming and smoldering states in areas of the fuel beds where fuels were tightly compacted and around larger woody particles. The fuel beds in this experiment were not of sufficient size to fully reach steady-state combustion; thus, the spread rates associated with the different moisture groups were only illustrative and thus were not reported. Average flame heights ranged from 12 cm in the 13–16% moisture group to 30 cm in the 4–8% fuel moisture group, visually indicating increased fire intensities at lower fuel moistures (Table 1). Flame heights were quite high during the initial spread of the fire across the burn platform, especially in the 48% and 10–12% fuel moisture groups, in

which flames heights were occasionally  $>1$  m, and then proceeded to slowly decline once the initial surface biomass was burned over. Our observed flame heights were within the range of flame heights measured in other studies burning masticated fuels in field and controlled settings (26–188 cm) [Bradley *et al.*, 2006; Busse *et al.*, 2005; Knapp *et al.*, 2011]. Flames advanced rapidly across the burn platform for the 4–8% fuel moisture group, whereas flames advanced much more slowly for the 10–12% moisture group and slowest for the 13–16% moisture group. Total flaming time was greatest in the 13–16% fuels, in which the flames advanced across the fuel beds at a slower rate and also sustained flaming combustion for extended periods in areas where fuels were more compacted on the burn platform. Smoldering times were highly variable and were not significantly different in the ANOVA results but do indicate that on average, smoldering combustion was greatest in the wetter (13–16%) fuel beds. The variability within smoldering combustion times can be attributed to the presence or absence of tightly compacted portions of the fuel bed within the burn platform area. In spite of the observed effects of fuel moisture on the flaming fire behavior, smoldering combustion was an important contributor to the overall consumption, and mass was qualitatively observed to diminish after flaming combustion had ceased.

[19] Constructing and burning “natural” fuel beds in a laboratory study have inherent limitations, inasmuch as fire behavior in wildland fires is affected by numerous dynamic fuels, weather, and topographical variables that change both temporally and spatially. Of potential importance in this study is the fact that the experimental fuel beds maintained consistent fuel moisture and did not exhibit differential moisture by depth, which is likely not the case for litter and duff horizons in naturally occurring surface fuels. Additionally, the lack of a duff horizon could potentially influence fuel bed consumption because both duff depth and moisture have been shown to be primary variables dictating woody fuel consumption in logging-slash fuel types [Brown *et al.*, 1991]. Despite these potential limitations, this experimental approach provides an improved understanding of the combustion dynamics that occur during combustion within specific wildland fuel types.

### 3.2. Post-fire Residues

[20] Once fire had established in the masticated fuel beds, it sustained the combustion reaction until nearly 90% of the fuel bed was consumed regardless of moisture group (Table 2). Although total fuel bed consumption did not significantly differ in our statistical analysis as a function of fuel moisture, the average post-fire residue mass in the 13–16% fuel moisture group was slightly higher than the average weight of the two drier fuel moisture groups. Weight of the total post-fire residues and residues by size class also did not vary as a function of fuel moisture (Figure 1a). Charred residue production for the three moisture groups was 9.60%, 8.78%, and 10.22% for the 4–8%, 10–12%, and 13–16% fuel moisture groups, respectively (Table 2). Charred residue production results are slightly higher than those of two other studies in temperate forest types, in which charcoal conversion rates were 5.1% for a slash-and-burn experiment and 8.0% in coarse, woody debris in Yellowstone National Park, USA [Eckmeier *et al.*, 2007; Tinker and Knight, 2001]. Differences between these studies and the results presented here are likely a function of several factors, including fuel loading and arrangement of the masticated fuels and resulting fire behavior. Also, our results include soot and ash, which accounted  $\sim 40\%$  of the total residue mass.

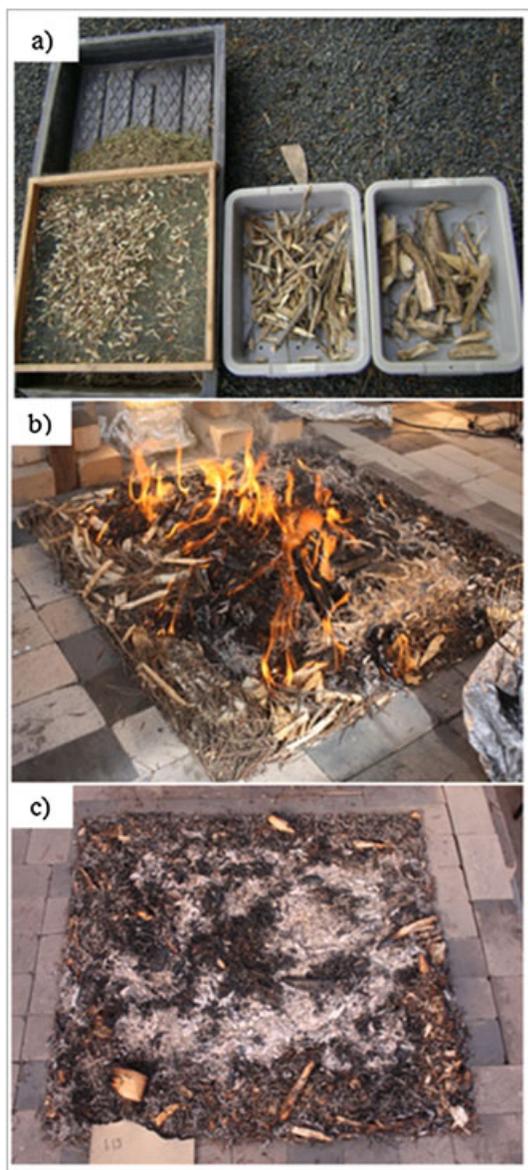
[21] Within the post-fire residues, a slight majority of the mass was allocated in the  $<1$  mm and  $>6$  mm size classes (greater than  $\sim 200$  g $^{-2}$ ) across all moisture groups, indicating that the majority of the pine needles and woody particles were either volatilized or fragmented to  $<1$  mm (Figure 2a and Table 3). Residues produced in the two lower fuel moisture groups (4–8% and 10–12%) maintained the greatest proportion of the total fuel bed mass in the  $<1$  mm size (soot and ash), whereas the majority of mass preserved in the 13–16% fuel moisture group was allocated in the larger charred, woody chunks  $>6$  mm, indicating more complete combustion at lower fuel moistures. In a few instances, charring did not penetrate the inner core of the larger masticated pieces, most notably in the 13–16% moisture group, similar in appearance to the conceptual model of charring proposed

**Table 2.** Mean (SD) Pre- and Post-Fire Mass, PyrC, Soot-BC, and Soot-BC:PyrC Characteristics ( $n = 5$  for each moisture level)<sup>a</sup>

Biomass Type	Moisture Group	Pre-fire (g m $^{-2}$ ) <sup>b</sup>	Post-Fire (g m $^{-2}$ )	Consumption (%)	Production (%)
Residue mass	4–8%	5668.26 (148.44)	571.65 (155.93)	90.39 (2.73)	9.60 (2.73)
	10–12%	5764.78 (106.26)	493.84 (107.34)	91.31 (1.85)	8.78 (1.95)
	13–16%	5932.45 (184.50)	622.47 (183.94)	89.71 (2.93)	10.22 (3.38)
<i>p</i> -value		—	0.904	0.622	0.623
PyrC	4–8%	2739.75 (71.75)	200.63 (60.64)	91.33 (2.73)	8.67 (2.63)
	10–12%	2786.41 (51.36)	243.68 (72.81)	92.77 (2.13)	7.23 (2.13)
	13–16%	2815.79 (89.18)	252.32 (91.4)	91.46 (3.00)	8.54 (3.00)
<i>p</i> -value		—	0.533	0.667	0.638
Soot-BC	4–8%	2739.75 (71.75)	0.44 (0.10) a	100 (0.00) a	0.02 (0.00) a
	10–12%	2786.41 (51.36)	0.58 (0.25) a	100 (0.00) a	0.02 (0.01) a
	13–16%	2815.79 (89.18)	1.42 (0.42) b	99.99 (0.00) b	0.05 (0.01) b
<i>p</i> -value		—	$<0.001$	$<0.001$	$<0.000$
Soot-BC:pyrC	4–8%	—	1.88E–03 (5.80E–04) a	—	—
	10–12%	—	4.31E–03 (2.54E–03) a, b	—	—
	13–16%	—	6.59E–03 (3.65E–03) b	—	—
<i>p</i> -value		—	0.019	—	—

<sup>a</sup>*p*-values for ANOVA results between moisture levels are shown when applicable. Homogenous subsets from Tukey’s post-hoc analysis identified by a, b, and c ( $\alpha = 0.05$ ).

<sup>b</sup>Pre-fire fuel loadings are shown for the residue mass. Pre-fire OC is shown for PyrC and soot-BC, calculated by multiplying carbon concentrations (%) by the dry weight.



**Figure 1.** Photographs showing (a) fuel bed construction and sorting of the individual size classes, (b) a masticated fuel bed during flaming combustion, and (c) post-fire residues.

by Donato *et al.* [2009]. It was observed that these partially burned pieces tended to reside near the fuel bed surface, where heating was not sustained. This phenomenon might also have been due to individual particles either having slightly higher moisture contents or the particles being extremely dense (i.e., knots). Particle size distributions of the residual material indicate that at higher fuel moistures, the masticated woody particles only partially combusted and did not fully volatilize or fragment into smaller sizes, unlike masticated fuels burned under drier conditions.

### 3.3. Pyrogenic Carbon

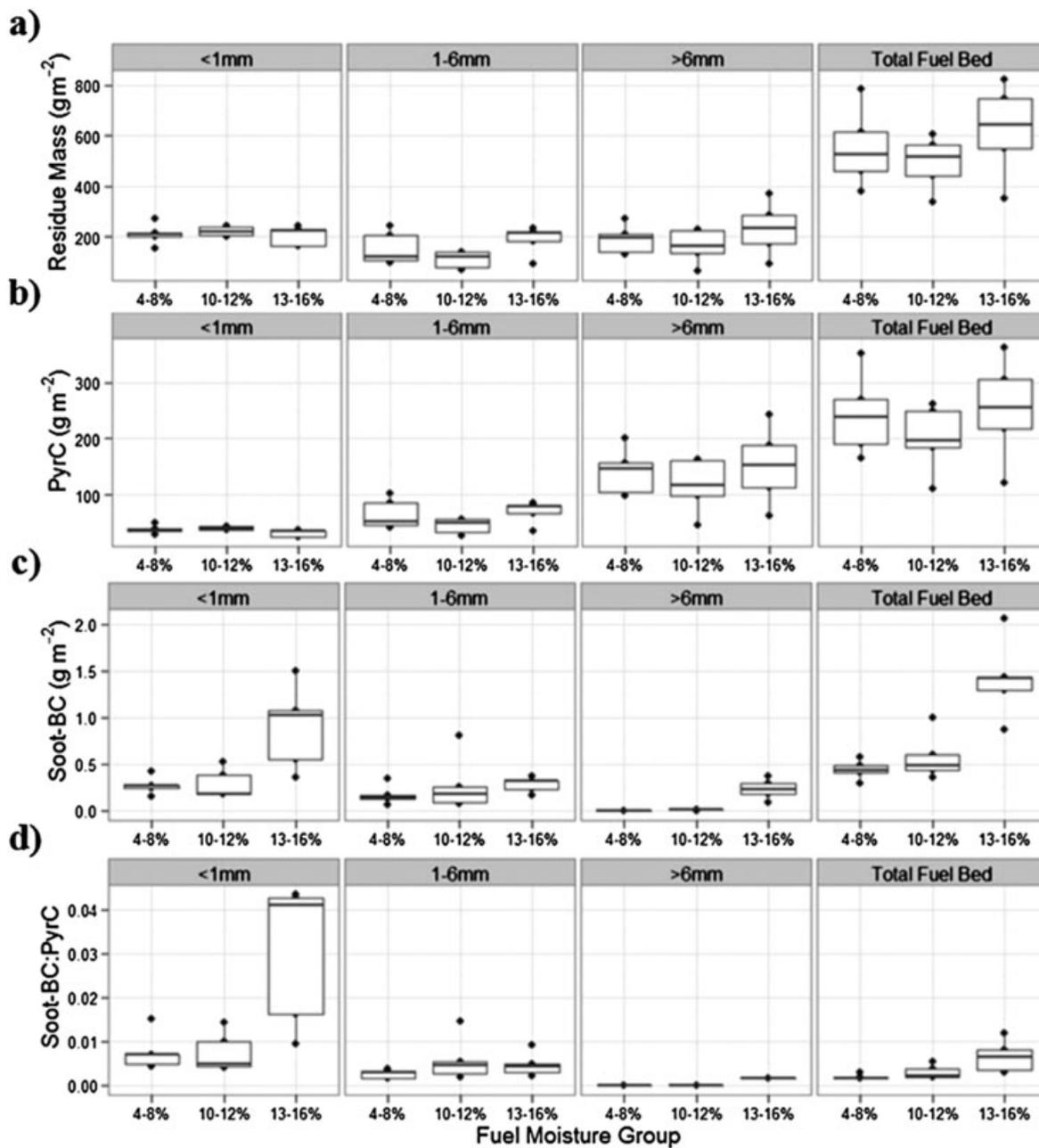
[22] Unburned OC concentrations for the pine needles and woody particles averaged 49.15% and 48.55% ( $n = 15$ ), respectively (Table 4). PyrC concentrations were particle size dependent with concentrations ranging from 15.37%

to 17.95% in the <1 mm residues, from 36.93% to 42.02% for the 1–6 mm residues, and from 65.73% to 74.45% in the >6 mm particles (Table 3). The relative lack of pyrC in the <1 mm size class is likely a function of the high ash content present in this size class and also shows that the size of the residues strongly influences the “nature” of the pyrC produced [Nocentini *et al.*, 2010]. Regardless of size, pyrC concentrations were slightly lower in the 13–16% moisture group relative to the 4–8% and 10–12% groups. The increased concentrations of pyrC with lower fuel moisture in the large residues (>6 mm and 1–6 mm size classes) are likely due to increased loss of oxygen and hydrogen from the molecular structure of char with increasing fire severity [Keilueit *et al.*, 2010].

[23] Similar to the trends in concentration, most of the pyrC produced was allocated in the larger particles (>6 mm), with the least amount of pyrC located in the soot and ash (<1 mm) residues (Figure 2b). Average pyrC production in the post-fire residues for the three moisture classes ranged from 200.63 to 243.68 to 252.32  $\text{g m}^{-2}$  for the 4–8%, 10–12%, and 13–16% moisture groups, respectively (Table 2). Although there were no significant differences in pyrC production among the fuel moisture groups, pyrC production generally increased with fuel moisture; this was largely due to slightly higher residue mass remaining in the 13–16% moisture group following combustion (Figure 2b). Conversion rates of the pyrC relative to pre-fire OC range from 7.23% to 8.54% (Table 2). When rates are normalized by total pre-fire dry weight, pyrC production ranges from 3.52% to 4.22% (data not shown). Previous studies reporting charcoal C production relative to pre-fire mass ranged from 1.0% to 4.8%, and our results compare well with these findings [Alexis *et al.*, 2007; Eckmeier *et al.*, 2007; Fearnside *et al.*, 1999, 2001]. Within the range of charcoal C production, fuel types containing high loadings of coarse, woody debris (>7.6 cm in diameter) produced less charcoal C, ranging from 1% to 3% because the large particles were not entirely consumed [Fearnside *et al.*, 1999, 2001]. Fuel types with greater amounts of small diameter (<7.6 cm) woody biomass produced charcoal C at slightly higher rates of 3.2–4.8% because the residues were more completely charred [Alexis *et al.*, 2007; Eckmeier *et al.*, 2007].

### 3.4. Soot-BC

[24] Soot-BC concentrations were one to 2 orders of magnitude lower than pyrC concentrations due to the removal of OC and inorganic carbonates prior to elemental analysis (Table 4). Soot-BC concentrations were highly variable both between size classes and across moisture groups, ranging from 0.03% to 2.65% (Table 4). This high variability is likely due to the heterogeneous nature of the fuels and the subsequent combustion environment within replicates, and standard deviations within the replicates ranged from 0.004 to 0.147. In all instances, the 13–16% moisture group contained the highest concentrations of soot-BC, indicating that fuel moisture affected the composition of the highly resistant soot-BC formed from the masticated fuels. The most dramatic difference in soot-BC concentrations was observed in the large charred particles, for which where concentrations ranged from 0.03% in the 4–8% moisture group to 2.65% in the 13–16% moisture group.



**Figure 2.** Post-fire components by moisture group and size class. (a) Residue mass. (b) PyrC production. (c) Soot-BC production. (d) The soot-BC to pyrC ratio.

[25] Total fuel bed soot-BC production increased from 0.44 and 0.58  $\text{g}^{-2}$  in the 4–8% and 10–12% moisture groups to 1.42  $\text{g}^{-2}$  in the 13–16% moisture group (Figure 2c and Table 2). Relative to the pre-fire OC conversion rates ranged from 0.02% to 0.05%. Previous studies analyzing BC production have reported production rates of 0.7% in boreal forests (using benzenepolycarboxylic acids (BPCA) as molecular markers) [Czimczik *et al.*, 2003] and 0.6–1.5% in subtropical savannahs (through and chemothermo-oxidation methods) [Kuhlbusch *et al.*, 1996], which are one to two orders of magnitude greater than production rates observed in the present study. Differences in observed production rates can be attributed partially to methodological differences, given that BPCA methods were shown to detect higher

concentrations of BC in wood char relative to CTO-375 methods [Hammes *et al.*, 2007]. OC removal methods for the charred residues used in Kuhlbusch and Crutzen [1995] utilized a less severe thermal pretreatment in which samples were heated to 340 °C for only 2 h. Additionally, the subtropical savannah grass fuels were shown to produce high amounts of ash residues <0.63 mm (~80% of the post-fire residues), which contained high amounts of BC [Kuhlbusch *et al.*, 1996], whereas ash residues <1 mm produced in our study comprised only ~40% of the total post-fire residues.

[26] The significant increase in soot-BC production at the 13–15% moisture level was affected primarily by the relatively large amount of soot-BC distributed in the ash residues <1 mm, although there were also increases in

**Table 3.** Mean (SD) Post-Fire Residue Size Class Distribution for Residue Mass, PyrC, Soot-BC, and Soot-BC:pyrC Ratios ( $n = 5$ )<sup>a</sup>

Biomass Type	Moisture Group	Size Class		
		<1 mm (g m <sup>-2</sup> )	1–6 mm (g m <sup>-2</sup> )	>6 mm (g m <sup>-2</sup> )
Residue mass	4–8%	210.06 (42.23)	154.00 (64.80)	189.74 (56.75)
	10–12%	220.98 (19.72)	109.56 (33.14)	163.30 (68.43)
	13–16%	203.68 (38.21)	188.42 (56.29)	230.37 (105.51)
<i>p</i> -value		0.735	0.103	0.433
PyrC	4–8%	39.65 (3.54)	43.96 (13.3)	117.02 (49.04)
	10–12%	37.7 (7.58)	64.72 (27.23)	141.26 (42.26)
	13–16%	31.31 (5.87)	69.58 (20.79)	151.42 (69.35)
<i>p</i> -value		0.105	0.171	0.607
Soot-BC	4–8%	0.27 (0.10) a	0.17 (0.10)	1.73E–03 (5.18E–04) a
	10–12%	0.29 (0.16) a	0.28 (0.30)	1.07E–02 (4.47E–03) a
	13–16%	0.9 (0.46) b	0.28 (0.08)	2.34E–01 (1.07E–01) b
<i>p</i> -value		0.006	0.58	<0.001
Soot-BC:pyrC	4–8%	7.65E–03 (4.33E–03) a	2.59E–03 (1.03E–03)	1.23E–05 (2.07E–21) a
	10–12%	7.48E–03 (4.57E–03) a	5.80E–03 (5.16E–03)	9.12E–05 (1.66E–20) b
	13–16%	3.05E–02 (1.64E–02) b	4.66E–03 (2.76E–03)	1.54E–03 (1.57E–21) c
<i>p</i> -value		0.005	0.356	<0.001

<sup>a</sup>*p*-values for ANOVA results between moisture levels are shown. Homogenous subsets from Tukey’s post hoc analysis identified by a, b, and c ( $\alpha=0.05$ ).

**Table 4.** Mean (SD) Pre-Fire OC ( $n=15$ ), PyrC ( $n=5$ ), and Soot-BC ( $n=5$ ) Concentrations (%) by Size Class for Each Fuel Moisture Level<sup>a</sup>

Concentration Type	Moisture Group	<1 mm	1–6 mm	>6 mm
Unburned OC (%) <sup>b</sup>	na	na	48.55 (0.10)	49.15 (0.69)
	4–8%	17.94 (2.73)	40.13 (8.82)	71.66 (4.66) a
	10–12%	17.95 (2.17)	42.02 (3.55)	74.45 (0.63) a, b
	13–16%	15.37 (3.59)	36.93 (8.52)	65.73 (0.83) b
<i>p</i> -value		0.495	0.708	0.021
Soot-BC (%)	4–8%	0.14 (0.07) a	0.30 (0.15)	0.03 (0.00) a
	10–12%	0.13 (0.08) a	0.45 (0.50)	0.22 (0.14) a
	13–16%	0.49 (0.27) b	0.51 (0.37)	2.65 (0.15) b
<i>p</i> -value		0.006	0.654	<0.001

<sup>a</sup>*p*-values for ANOVA results between moisture levels are shown. Homogenous subsets from Tukey’s post hoc analysis identified by a, b, and c ( $\alpha = 0.05$ ).

<sup>b</sup>Pre-fire OC values for the pine needles and woody particles are shown in the 1–6 mm and >6 mm columns, respectively.

soot-BC production in the 1–6 mm and >6 mm residues for the 13–16% moisture group as well. In contrast to pyrC production, the majority of soot-BC was allocated in the <1 mm size fraction (0.27, 0.29, and 0.90 g m<sup>-2</sup> for the 4–8%, 10–12%, and 13–15% fuel moisture groups, respectively), suggesting that a portion of these fine residues was likely formed through the re-condensation of volatiles at high combustion temperatures as opposed to less resistant pyrC formed at lower temperatures [Preston and Schmidt, 2006]. The larger (>6 mm) charred particles, although high in pyrC, contained the least amount of soot-BC relative to the other size classes (from 0.002 to 0.007 g m<sup>-2</sup>). These results suggest that the fire did not achieve temperatures required to convert the OC to soot-BC for conversion toward the interior of the macro-size woody particles.

[27] Soot-BC production results presented here are counterintuitive to the prevailing hypothesis that higher fire intensities produce greater amounts of highly thermally altered (e.g., more resistant to biologic degradation) pyrC and soot-BC [Hatten and Zabowski, 2009; Keiluweit et al., 2010]. Although char samples can be produced in the laboratory under specific combustion conditions [Bruun et al., 2008; Nguyen et al., 2010], wildfire temperatures and conditions (even when simulated in the laboratory) are not as clearly defined. Our results suggest that at some threshold value of fire intensity (observed here to be between the

10–12% and 13–16% moisture levels), the aromatic precursors to soot-BC were indiscriminately consumed and were not retained in the post-fire residues. Further research that explores and further defines this soot-BC retention/loss “threshold” concept in complex wildland fuel types and fire conditions is clearly needed.

[28] The relative degree of resistance of fire-altered residues to biological degradation may be evaluated using the ratio of soot-BC to pyrC [Hatten and Zabowski, 2009]. This assumes that the distribution of pyrC follows a continuum of unburned to soot-BC (i.e., turbostratic char) with all transition states in between along a normal distribution curve [e.g., Keiluweit et al., 2010]. This also assumes that the ratio of soot-BC to pyrC is representative of the average residue composition of pyrC (higher soot-BC:pyrC suggests more thermally altered and biologically stable molecular structures). The majority of soot-BC created in masticated fuels exists in the <1 mm size class, and this class of material also maintained the highest soot-BC:pyrC ratio, suggesting that residue size is important in the formation of soot-BC in masticated fuels. These findings support the findings of Glaser and Amelung [2003], who showed that the majority of BC found in the soil was in these smaller size classes (silt+clay), which may be resistant to degradation because of physical protection as well as biological and chemical resistance.

[29] With very low production rates of 0.02–0.05% (relative to pre-fire OC), soot-BC is likely not an important contributor to stand-level soil soot-BC in the short term (e.g., one fire event). On the other hand, pyrC production rates of 8.78–10.22% of the surface biomass C represent a larger potential contribution to overall soil C; however, mean residence times associated with the entire range of pyrC structures have been hard to quantify [Schmidt *et al.*, 2011]. Over time, and multiple fire events, incorporation of pyrC and soot-BC into soils may slowly increase a stand’s long-term carbon pool if it can be sufficiently protected from future degradation mechanisms [Schmidt *et al.*, 2011]. Soot-BC deposition in marine sediments is a major potential sink for both anthropogenic and biomass-derived soot-BC [Sánchez-García *et al.*, 2012]. The contribution of biomass-derived soot-BC appears to be relatively minor compared to anthropogenic sources in more industrialized regions of the globe. Despite the application of CTO-375 procedures to measure soot-BC in sediments, this is one of the first studies that explicitly measured soot-BC production from biomass burning. Our results should begin to elucidate the relative contribution of soot-BC produced via biomass burning to overall soot-BC measured in marine sediments [Sánchez-García *et al.*, 2012].

**3.5. Fire-Altered Residue Composition**

[30] The largest pyrC:N ratio was observed in the >6 mm size class, with smaller ratios in the two smaller size classes (Table 5). These trends are similar to the unburned fuel C:N ratios, suggesting that physical fragmentation of the woody particles during combustion did not have a major effect on post-fire pyrC:N ratios. If even a small amount of the fuel particles was fragmented from a larger (e.g., >6 mm) size fraction to one of the smaller size fractions (e.g., 1–6 mm), there would likely have been a large increase in the C:N ratio of the smaller size classes. This hypothesis is supported by a lack of any substantial trend in the  $\delta^{13}\text{C}$  pyrC isotope data, given that variation in the isotope data is likely due to variability in the parent material [Bird and Ascoug, 2012].

[31] Irrespective of size class, pyrC:N ratios were less than unburned C:N ratios, indicating that regardless of fuel, moisture C was preferentially volatilized relative to N (Table 5). Increased fuel moisture decreased fire intensity, thus leading

to changes in the overall composition of the post-fire residues. Fuel moisture had a significant effect on pyrC:N in the >6 mm and <1 mm size classes, in which lower pyrC:N ratios were found at higher fuel moistures. There appeared to be more indiscriminate combustion of compounds at low fuel moistures, insofar as pyrC:N ratios trended closer toward those of unburned materials. A Pearson correlation analysis between the soot-BC:pyrC ratio and the pyrC:N ratio of the residue produced a moderate negative correlation of  $R = -0.602$  ( $p < 0.001$ ), suggesting that fire severity (using soot-BC:pyrC as a proxy) increased the relative rates of volatilization of C and N and that the pyrC:N ratio converged.

[32] The stable isotopic composition of the <6 mm fractions was lighter than that of the unburned material, suggesting that lignin (typically ~3‰ lighter than cellulose) was preferentially preserved or transformed into pyrC. The slightly, yet statistically significantly, heavier stable isotopic composition of the <1 mm fraction burned at the highest fuel moisture suggests that more carbon from cellulose was preserved relative to lignin in the higher intensity treatments. Similarly, soot-BC  $\delta^{13}\text{C}$  data in the >6 mm size class again support the idea of indiscriminate consumption at lower fuel moistures, with lignin and cellulose being preferentially removed at higher fuel moistures. We hypothesize that heavier isotopic composition and lower C:N ratios were the result of N thermally stabilizing pyrC at this higher fuel moisture and low burn intensity.

[33] Our results point to the concept that the presence of N in organic matter is important in the production of BC. Previous work has suggested that nitrogen provides stability to chars at temperatures under 450 °C and that C:N ratios increase with temperatures above this threshold [Knicker *et al.*, 2008; Knicker, 2010]. These trends are attributed to the thermal stability imparted by N and a preferential combustion of low-N-containing organic matter [Knicker *et al.*, 2008]. However, the N associated with pyrogenic materials is less recalcitrant than the associated C [de la Rosa and Knicker, 2011]. Despite increased resistance to thermal degradation, the presence of greater amounts of N may eventually lead to higher microbial decomposition rates. Our study is limited in these conclusions without some characterization of the molecular structure of the residue. However, this is one of a few studies in which materials

**Table 5.** Mean (SD) C:N and Isotope Values for Unburned PyrC and Soot-BC<sup>a</sup>

Biomass Type	Moisture Group	C:N			$\delta^{13}\text{C}$ Isotope (‰)		
		<1 mm	1–6 mm	>6 mm	<1 mm	1–6 mm	>6 mm
Unburned <sup>b</sup>	—	—	103.13 (16.21)	477.64 (52.37)	—	–26.74 (0.11)	–27.16 (0.09)
<i>n</i>	—	—	3	3	—	3	3
PyrC	4–8%	25.98 (0.53) a	39.26 (5.38)	371.32 (20.52) a	–27.69 (0.04) a	–27.86 (0.14)	–27.17 (0.14)
	10–12%	21.6 (0.5) b	39.84 (0.31)	227.45 (42.18) a	–27.71 (0.05) a	–27.92 (0.41)	–27.31 (0.98)
	13–16%	21.29 (1.02) b	36.89 (3.44)	187.36 (18.40) b	–27.36 (0.21) b	–27.93 (0.27)	–26.44 (0.04)
<i>n</i>		3	3	3	3	3	3
<i>p</i> -value		<0.001	0.611	0.001	0.023	0.948	0.214
Soot-BC	4–8%	4.47 (1.05)	4.51 (0.88)	0.37	–24.63 (1.33) a	–23.03 (0.27) a	–27.57
	10–12%	3.92 (1.45)	4.95 (1.41)	2.91	–24.16 (0.39) a	–23.07 (0.31) a	–23.54
	13–16%	10.05 (6.28)	4.52 (0.96)	12.16	–25.3 (0.88) b	–23.63 (0.3) b	–21.17
<i>n</i>		5	5	1	5	5	1
<i>p</i> -value		0.086	0.805	—	0.013	0.184	—

<sup>a</sup>Some replicates were merged within moisture groups, and sample sizes are indicated (*n*). *p*-values for ANOVA results between moisture levels are shown. Homogenous subsets from Tukey’s post hoc analysis identified by a, b, and c ( $\alpha = 0.05$ ).

<sup>b</sup>Unburned biomass values shown in the 1–6 mm and >6 mm columns represent unburned needles and woody particles, respectively.

produced under controlled burning conditions mimicked a natural fire, and we have demonstrated that there are processes at work under these conditions that create pyrC much different from that produced in isothermal heating experiments (e.g., muffle furnace).

#### 4. Conclusions

[34] The experimental approach used in this study allowed for a unique opportunity to control and replicate burns within a specific fuel type with identical fuel loadings and particle size distribution under fixed fuel moisture settings. The production of soot-BC and the elemental composition of our post-fire residues varied as a function of fuel moisture, with highest soot-BC production rates and soot-BC:pyrC ratios in residues burned at 13–16% fuel moisture. Fire intensity differences (as controlled by fuel moisture) are likely a key driver in soot-BC production and/or soot-BC volatilization in masticated fuels, in which dry fuel precursors to soot-BC were likely indiscriminately consumed at high fire intensities early in the combustion process. Fuels burned at higher fuel moistures likely preserved these precursors for the eventual conversion to soot-BC. With fuel moisture being an easily measurable fuels variable, management strategies emphasizing carbon retention should consider burning when fuel moistures are greater than 12% to maximize the soot-BC production, although the results presented here should be validated with further field testing.

[35] Future research to characterize fire behavior in masticated fuel beds and the associated fire effects, including pyrC and soot-BC formation, is essential. This is especially warranted in stands managed for multiple objectives in which both carbon retention and fuels reduction are favored. Recent events such as the Lower North Fork Fire escape in Colorado, 2012, highlights the lack of knowledge of fire behavior in masticated fuels, including duration of smoldering combustion. As noted earlier, very little research has been conducted in wildfire and prescribed fires to test how variations in specific fuel properties and weather characteristics influence fire behavior and subsequent production of pyrC and soot-BC within specific fuel types, and we contend that quantifying these variations will help provide a more robust accounting of the contribution of fire-affected material to global estimates. Given the inherent challenges of accurately measuring coincident pre-fire loadings, fire behavior measurements, and post-fire residues; an experimental approach similar to that conducted herein may prove useful.

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