

INFLUENCES OF FUEL MOISTURE AND REPEATED BURNING ON  
BLACK CARBON PRODUCTION AND LOSS IN MASTICATED FUELS:  
AN EXPERIMENTAL COMBUSTION STUDY

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## AUTHORIZATION TO SUBMIT THESIS

This thesis of Nolan W. Brewer, submitted for the degree of Master of Science with a major in Forest, Rangeland, and Fire Sciences titled “INFLUENCES OF FUEL MOISTURE AND REPEATED BURNING ON BLACK CARBON PRODUCTION AND LOSS IN MASTICATED FUELS: AN EXPERIMENTAL COMBUSTION STUDY” has been reviewed in final form. Permission, as indicated by the signatures and dates given below, is now granted to submit final copies to the College of Graduate Studies for approval.

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## Abstract

Forests have internationally been recognized as carbon sinks, and future forest management strategies should facilitate practices that improve their sink potential. Efforts to improve stand resilience in the Western U.S. utilize various fuels reduction techniques to remove or reallocate biomass from aerial fuels to ground fuels to reduce fire risk. Mastication (mechanized mulching) is commonly used to redistribute aerial ladder fuels to the forest floor. Prescribed fires often follow mastication treatments to reduce surface fuel loadings and reduce future extreme fire behavior; resulting in charred residues and ash due to incomplete and complete combustion respectively. Carbon in these fire-altered residues, commonly referred to as black carbon (BC), has prolonged residence times (ca. 1000-10,000 years) in terrestrial ecosystems due to changes in atomic structures brought about by thermal oxidation. Accumulation of BC in forest soils through multiple fire events can lead to a net increase a forest carbon stocks as successive fire disturbance/regeneration cycles occur over time if the BC is successfully passed into passive carbon pools. The persistence of BC in soils is a function of formation temperature, where higher formation temperatures produce highly biologically resistant BC. Very little BC research has been conducted in wildland fire environments addressing specific fuel properties which directly control fire behavior. Chapter 1 uses 15 masticated fuel beds set at three moisture levels to experimentally test how fuel moisture influences BC produced, effectively manipulating the fire intensity, in wildland masticated fuels. Increases in fuel moisture led to increased BC concentrations, while dryer fuel moisture produced less BC. These results suggest that fuel moisture and resulting fire intensity are important drivers of BC production. Following formation, several degradation

mechanisms act upon BC, including subsequent fire. However, loss rates associated with repeated burning have yet to be quantified. Chapter 2 tests BC loss rates of the > 6mm residues created in the initial burning of the 15 fuel beds through four repeated burns (a total of 60 fires). Greater than 99% of the black carbon produced in the initial fire is lost by the fourth repeated burn, suggesting that soil incorporation needs to occur faster than 3-4 times the mean fire return interval of a given ecosystem. Future research should evaluate incorporation rates of fire-altered residues, especially in high fire frequency ecosystems.

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## **Dedication**

This work is dedicated to my wife, Lyndsay, and my parents; this work is a reflection of all the love and support you have provided over the years. Thank you.

**TABLE OF CONTENTS**

<b>AUTHORIZATION TO SUBMIT THESIS</b>	<b>II</b>
<b>ABSTRACT</b>	<b>III</b>
<b>ACKNOWLEDGEMENTS</b>	<b>V</b>
<b>DEDICATION</b>	<b>VI</b>
<b>TABLE OF CONTENTS</b>	<b>VII</b>
<b>LIST OF FIGURES</b>	<b>VIII</b>
<b>LIST OF TABLES</b>	<b>X</b>
<b>CHAPTER 1</b>	<b>1</b>
<b>ABSTRACT</b>	<b>2</b>
<b>INRODUCTION</b>	<b>4</b>
<b>METHODS</b>	<b>8</b>
<b>RESULTS AND DISCUSSION</b>	<b>13</b>
<b>CONCLUSIONS</b>	<b>20</b>
<b>REFERENCES</b>	<b>24</b>
<b>CHAPTER 2</b>	<b>36</b>
<b>ABSTRACT</b>	<b>37</b>
<b>INTRODUCTION</b>	<b>38</b>
<b>METHODS</b>	<b>41</b>
<b>RESULTS AND DISCUSSION</b>	<b>43</b>
<b>CONCLUSIONS</b>	<b>47</b>
<b>REFERENCES</b>	<b>49</b>

**LIST OF FIGURES**

- FIGURE 1.1** Flow chart showing (a) fuel bed composition, (b) the completed fuel bed, and (c) post-fire residue size classes and carbon components. 28
- FIGURE 1.2** Fire radiative power flux points (n = 5 for each fuel moisture group) corresponding with the primary y-axis. Average integrated fire radiative energy (FRE) values are shown with lines, and correspond with the secondary y-axis. 29
- FIGURE 1.3** Post fire components by moisture group and size class, (a) residue weight, (b) pyrC production, (c) BC production, and (d) The BC to pyrC ratio. Outlier values >1 and >2 standard deviations away from the mean are shown by \* and ° respectively. 30
- FIGURE 2.1** Loss curves for the fire-altered macro charcoal particles, pyrogenic C, and black C. Curves were modeled using exponential regression through the formula:  $y = e^{(-kt)}$ . 52
- FIGURE 2.2** The black carbon to pyrogenic carbon ratio through the 5 repeated burns. The ratio decreases substantially on the 3<sup>rd</sup> burn, as black carbon is preferentially removed from the post-fire residues. 53
- FIGURE 2.3** Two hypothetical carbon budgets shown for post-fire residues, pyrogenic C and black C - one scenario with loss rates included, and the other without loss rates for post-fire residues, pyrogenic carbon, and black carbon (n =15). Loss rates are based on macro-charcoal particle loss through repeated burning. 54

## LIST OF TABLES

<b>TABLE 1.1</b> Mean (SD) fuel bed characteristics and ambient burn conditions for each fuel moisture category (n = 5 for each moisture category).	31
<b>TABLE 1.2</b> Fire characteristics by moisture levels (n = 5). Homogenous subsets identified by a, b, c ( $\alpha = 0.05$ )	32
<b>TABLE 1.3</b> Mean (SD) pyrC and BC concentrations (%) for each fuel moisture groups. ANOVA comparisons were analyzed across moisture groups (n = 3 for pyrC, and n = 5 for BC). Homogenous subsets from Tukeys post-hoc analysis identified by: a, b, c ( $\alpha = 0.05$ ).	33
<b>TABLE 1.4</b> Mean (SD) for post-fire residues, pyrC, BC, and the BC:pyrC ratio for each size class of post-fire material, as well as the total combined fuel bed. ANOVA was used to analyze differences across moisture levels. Homogenous subsets are indicated by: a, b, c as tested by Tukeys post-hoc test ( $\alpha = 0.05$ ).	34
<b>TABLE 1.5</b> Mean (SD) C:N and $\delta^{13}\text{C}_{\text{VPDB}} \times 1000$ isotope values for pyrC and BC by residue size (n = 3 for pyrC, n = 5 for BC). Unfortunately too little sample remained to gather standard deviations for values of BC > 6mm. ANOVA was used to test for differences across moisture level, homogenous subsets are identified by: a, b, c from Tukeys post-hoc analysis ( $\alpha = 0.05$ ).	35

**TABLE 2.1** Mean (SD) fuel bed characteristics and burn conditions for the burns (n = 15 for each burn number). 55

**TABLE 2.2** Mean (SD) rates for the post-fire residues, pyrogenic C, and black C and associated loss rates (n=15) for the > 6mm charred residues. A repeated measures ANOVA was used ( $\alpha= 0.05$ ), and homogenous subsets marked by: a,b,c as identified by Bonferonni post-hoc analysis. Unstandardized slope coefficients (se) and  $R^2$  for exponential regression analysis are also shown. 56

**TABLE 2.3** Pyrogenic C (n=9) and black C (n=3) characteristics through 5 repeated burns and p-values associated with repeated measures ANOVA ( $\alpha = 0.05$ ). Homogenous subsets marked by: a,b,c as identified by the Bonferonni post-hoc test. 57

## Chapter 1:

Fuel Moisture Influences on Fire-altered Carbon in Masticated Fuels: An Experimental Study

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**Abstract:**

Biomass burning is a significant contributor to atmospheric carbon emissions, but may also provide an avenue for fire-affected ecosystems to potentially increase soil carbon stocks over time, through the production of decomposition resistant fire-altered carbon in the post-fire residues. Land managers forests often employ mechanical thinning, or mastication, to reallocate aerial fuels to the forest floor to reduce the risk of crown fire and surface fire which improves stand resilience to future disturbance events. The mastication treatment is often followed by prescribed fire to decrease surface fuel loadings in these stands.

Understanding how fuel moisture, and subsequent changes in combustion dynamics, relates to the production of fire-altered carbon is important in determining how persistent charred residues are in soils following a fire. In this experimental study, fifteen masticated fuel beds conditioned to three fuel moisture ranges were created to compare production rates of pyrogenically-altered carbon and black carbon. Pyrogenic carbon was determined through elemental analysis and black carbon was quantified using thermo-chemical methods. Using a dual-band spectro-radiometer, fire radiative energy was measured for the 4-8% and 13-15% fuel moisture groups. Fire radiative energy was shown to be negatively correlated with black carbon production. Pyrogenic carbon production rates ranged from 7.23 to 8.67% relative to pre-fire organic carbon content across all fifteen fuel beds. However, black carbon production rates averaged 0.02% in fuel beds with 4 to 8% fuel moisture, up to 0.05% in the 13-18% fuel moisture group. A comparison of the ratio of black carbon to pyrogenic carbon indicates that burning in fuels ranging from 13-15% moisture content resulted in a higher proportion of black carbon produced, suggesting that the precursors to black carbon are indiscriminately consumed at lower fuel moistures, which produced higher fire intensities.

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. Through the incorporation of fire radiative energy, future remote-sensing-based carbon assessments may start to include black carbon estimates. Further assessment of fuel moisture is also warranted in other fire-prone ecosystems.

## 1. Introduction

Forested terrestrial ecosystems have recently received attention for their potential role in sequestering carbon to help offset global greenhouse gas emissions from fossil fuel and biomass burning [Malhi *et al.*, 2002]. As a result of this attention, policy and management efforts are currently being encouraged to include carbon at the stand scale [Canadell and Raupach, 2008]. Carbon cycling in fire-prone forests is inherently complex due to numerous factors acting on the stand over time [McKinley *et al.*, 2011]. In a given forest stand, biomass accumulation periods (carbon sink as above ground carbon pools grow) are often followed by a disturbance processes, e.g., land conversion, harvesting, fire, insects, wind, etc. 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 remaining after a fire, commonly referred to as BC [DeLuca and Aplet, 2008]. This thermally altered BC (BC) have the potential to persist in terrestrial soils for thousands of years, thereby slowly increasing a forest soil carbon stocks over multiple fire events [DeLuca and Aplet, 2008].

Throughout the forests of the Western United States, successful fire exclusion policies have led to large increases in biomass accumulation [Agee and Skinner, 2005]. In many of these fire-affected forest systems, thinning and prescribed fires are commonly used to reduce excessive build-up of fuels [Agee and Skinner, 2005]. These management practices

actively remove above-ground carbon in order to maintain ecosystem function and increase stand resilience to future disturbance, an increasingly important goal in the face of climate change and increased fire frequencies [Westerling *et al.*, 2006]. Mastication is an increasingly common forest thinning treatment in which a tracked or wheeled excavator mounted with a rotating head or drum grinds down smaller trees and shrubs, effectively reallocating aerial fuels to the forest floor [Battaglia *et al.*, 2010]. Oftentimes prescribed fire treatments are employed following mastication to reduce surface fuel loadings, and to further reduce the threat of high-intensity wildfire [Agee and Skinner, 2005].

The impacts 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 serve to reduce short-term stand-level carbon stocks, studies have found that fuels reduction may actually increase stand-level carbon over time, as large diameter trees store a disproportionately large amount of above-ground carbon [Hurteau and Brooks, 2011]. At the landscape level it is expected that forest carbon will generally decline with thinning and burning efforts [McKinley *et al.*, 2011; Reinhardt and Holsinger, 2010]. Given these contrasting results, carbon sequestration in managed forests should be considered an “ancillary benefit,” and some have suggested that future management efforts designed for carbon retention should allow for continuous disturbance processes to occur over time [Hurteau and Brooks, 2011]. BC and other fire-altered residues have yet to be effectively incorporated in these stand-level carbon budgets, yet this may contribute to a slowly growing passive carbon pool in forest soils through the continued application of prescribed burning [Hurteau and North, 2009]. Another potential source of BC in managed forest soils is the

addition of biochar, which is a primary byproduct from pyrolysis energy production [Lehmann, 2007].

Carbon in fire-altered residues exists on a continuum, ranging from partially-charred plant material to re-condensed soot and BC [Masiello, 2004; Preston and Schmidt, 2006]. 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” simply refers to the material following a fire ( $\text{g m}^{-2}$ ). Due to inconsistencies in fire-altered carbon quantification procedures, the present study differentiates between pyrogenic carbon and black carbon, in order to distinguish the highly recalcitrant portion of the fire-altered carbon (Figure 1.1) [Keiluweit et al., 2010]. The term “pyrogenic carbon” (pyrC) refers to all fire-altered carbon in the post-fire residues, regardless of its resistance to degradation mechanisms. BC is defined as the highly resistant portion within the pyrC below. Due to its thermally altered chemical structure, black carbon is believed to be highly resistant to degradation mechanisms once incorporated into forest soils [Preston and Schmidt, 2006]. Furthermore, the degree of alteration in the chemical structure of the black carbon is dependent upon primarily fire temperature but heating duration also plays a role at lower burning temperatures, combined these factors are also known as charring intensity [Czimczik and Masiello, 2007; Keiluweit et al., 2010].

Charring intensity dictates the chemical structure of BC, and has been related to degradation rates of BC in laboratory settings [Nguyen et al., 2010]. During burning both aromatic (e.g. lignin) and non-aromatic (e.g. cellulose) compounds contribute to the formation of pyrogenic carbon [Shafizadeh, 1984]. However, fuels with high lignin-to-

cellulose ratios produce greater amounts of BC probably as a result of the precursor having a similar chemical structure to the pyrogenic carbon [Czimeczik *et al.*, 2005]. While much research on black carbon formation has been conducted in laboratory settings, research conducted in wildfire and prescribed fire settings is limited, with very little research available accurately characterizing the mechanisms associated with its formation, such as pre-fire fuel conditions and fire intensity measurements [Czimeczik and Masiello, 2007]. This knowledge gap is likely due to the inability to isolate and test variables in the field which likely affect the formation of fire-altered carbon. Further research is necessary to better account for the mechanisms occurring in the fire-altered biomass in wildland fire settings [Forbes *et al.*, 2006].

While BC is present in all fire-affected ecosystems, BC research has primarily focused within the boreal regions, temperate savannas, and tropical rain forests, with very few studies evaluating BC production in the temperate forest types of the Western United States [Donato *et al.*, 2009; Tinker and Knight, 2001]. In these forest types, fuel moisture is a key component dictating fire behavior, fire severity, and influencing post-fire ecological effects. To our knowledge no studies exist that evaluate the effects of fuel moisture on BC production, or the production of BC in masticated wildland fuels in dry temperate forests. Given that BC formation and the degree of thermal alteration is driven by charring intensity, it is likely that fuel moisture in wildland fuels will influence both the quantity of BC formed, as well as resistance to degradation of the BC produced. Research is warranted that accurately quantifies the conversion rates of biomass to BC in both managed and naturally occurring fuel types, as well as how specific particle characteristics (e.g. fuel moisture)

influence the conversion process and ultimately the longevity of the post-fire charred materials generated in the fire event.

The current study evaluates how fuel moisture affects the conversion of masticated biomass to pyrC and BC. Previous carbon studies in masticated fuels have focused primarily on how fuel treatments influence changes in above-ground carbon pools, and found little change in soil carbon following treatments [Stephens *et al.*, 2009]. However, these studies did not incorporate the conversion of biomass to BC, and acknowledge that BC may increase a stand's soil carbon pool over time [Hurteau and North, 2009].

In response to these needs, an experiment was designed to evaluate the role of moisture content on the production of BC in masticated fuels, representative of a mixed conifer stands commonly found throughout the interior Western United States. We conditioned 15 masticated fuel beds to three fuel moisture groups (4-8%, 10-12%, and 13-16% by dry weight) to simulate the range of fuel moistures that exist in temperate dry forests of the Western United States in a mixed conifer stand. The objectives of this study were to (1) quantify the pyrC and BC in masticated fuels under the three pre-set fuel moisture groups, (2) evaluate the relative degree of resistance to degradation of the fire-altered carbon, and (3) explore the utility of fire radiative energy measurements to infer BC formation.

## **2. Methods**

### **2.1 Fuel Bed Construction**

An 8-ha mixed conifer stand, comprised of white pine (*Pinus monticola*) and Douglas-fir (*Pseudotsuga menziesii*) ingrown with lodgepole pine (*Pinus contorta*), on 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 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 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). Using 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 area. All fuels within the quadrat were removed to mineral soil, placed in a bag, and transported back to the University of Idaho's Fire Laboratory (IFire). Due to 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, and 0.6 - 0.3 cm, and needles), 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 slightly lower than to masticated fuel loadings in mixed conifer stands measured in Colorado [Battaglia *et al.*, 2010].

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 the construction of the experimental fuel beds. Fifteen fuel beds were assembled by recombining the sorted particles, using estimates of average dry weights of each size class. Replicates of five fuel

beds were designated to one of three pre-determined moisture levels of 3-8%, 10-12%, and 13-16%; fuel moisture was measured as a proportion of the dry weight.

The pre-constructed fuel beds were stored in a chamber with average fuel moistures ranging from 10-12%. The five fuel beds to be dried to 3-8% were taken from the control chamber the day of the burn trial and were dried in a convection oven for 4 hours at 37.5 °C, to simulate the temperature conditions similar to those of a hot summer day in the Northern Rockies when a wildfire might occur. The five fuel beds to be burnt at the 13-16% level were exposed to ambient conditions during the spring months of March and April to simulate conditions which 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 similar to the fuel beds ( $n = 10$  for each size class of the fuel bed).

Masticated wood particles and pine needles were sampled for organic carbon (OC) content. The unburnt fuels were milled in a grinder, dry sieved through a 500  $\mu\text{m}$  mesh screen, and analyzed for C and N through processes described below. Pre-fire organic carbon content for the organic matter was calculated by multiplying the %OC data for the needle and wood by the mass of the fuel bed ( $\text{g m}^{-2}$ ). This study only included surface organic matter and not the mineral soil horizon, as we did not wish to contaminate our samples with mineral soil [Forbes *et al.*, 2006].

## 2.2 Active Fire Measurements

All burn trials were conducted at the IFire Laboratory. The fuel bed was thoroughly mixed in a large bin for one minute, spread onto the burn table over the 0.37  $\text{m}^2$  area, and compressed by hand to achieve the average fuel bed height observed in the field.

Temperature and relative humidity readings were recorded every five minutes throughout the

trial with a Kestrel<sup>®</sup> 3000 pocket weather meter to validate that ambient conditions were not responsible for differences in fire behavior (Table 1.1). A dual band spectrometer was placed over the fuel bed and fire radiative power (FRP,  $\text{W m}^{-2}$ ) was logged at five second intervals throughout the burn trial. In addition, the fuel beds were burnt on a Sartorius EB Series scale (Goettingen, Germany), synchronized with the spectrometer to log mass loss throughout the burn period. To minimize the effects of unwanted conductive heat transfer through the surface of the scale a  $0.37 \text{ m}^{-2}$  3000°F Ceramic Board (Cotronics Corp, Brooklyn, NY) was placed over the scale. Masticated fuels were placed directly on this board for burning to ensure that post-fire residue measurements were not contaminated by in-situ soil, unlike prior studies which were burnt on sand [Wooster *et al.*, 2005]. Measurements from the dual-band spectrometer sensor and scale were then initiated and allowed time to calibrate to ambient conditions. For ignition, a small amount of lighter fluid was added to a strip of excess material surrounding the area of observation, which was then ignited and allowed to carry the flame through the area of observation. Once ignited, flame heights, flaming time, and smoldering time were recorded for each experimental trial, with the burn trial considered complete once mass loss ceased.

### **2.3 Post-Fire Residue Analysis**

Several measurements were used to characterize the post-fire residues. Residue mass (g) was first established by weighing post-fire materials immediately following the burn trial. Residues were then dry sieved into 3 size classes (< 1mm, 1-6mm, and > 6mm) and weighed, as the composition of each size class was likely to vary as a function of parent materials [Nocentini *et al.*, 2010]. Two samples were taken from each size class for further analysis, one for pyrC and the other for BC analysis (Figure 1.1). The concentrations of organic

carbon (OC) 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. 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) [Brenna *et al.*, 1997; Qi *et al.*, 2003]. Isotopic reference materials were interspersed with samples for calibration. Contribution of  $\text{O}^{17}$  was corrected by the IRMS software using the Santrock correction [Santrock *et al.*, 1985]. PyrC concentration (%C) of the residue was multiplied by the mass ( $\text{g m}^{-2}$ ) of the post-fire residue to calculate pyrC production for each of the fuel beds ( $\text{g m}^{-2}$ ).

The second sample was analyzed for BC using an adapted two-step thermo-chemical method outlined in Gustafsson *et al.*, [1997] and Hatten and Zabowski [2009]. Samples were dried at  $100^\circ\text{C}$ , weighed, spread evenly across the bottom of a 35-mm ceramic crucible, and placed in a pre-heated muffle furnace at  $375^\circ\text{C}$  for 20 hours to remove any organic, non-recalcitrant carbon. Care was taken to maintain a sample thickness of  $< 1\text{mm}$  to prevent additional pyrolysis from occurring in the muffle furnace. Samples were then treated with 6N HCl to remove any carbonates that may remain in the sample. Following the thermo-chemical treatment, the samples were elementally analyzed, using the same methods as described above for pyrC, for BC and black nitrogen (BN) concentrations (%), and  $\delta^{13}\text{C}$  isotope determination. BC 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, and then by the mass of the post-fire residue.

The ratio of BC to pyrC then provided a proxy to determine the relative biologic recalcitrance of the post-fire carbon [Hatten and Zabowski, 2009]. Results were also

normalized by pre-fire organic carbon content to determine pyrC and BC production rates. Inclusion of isotopic and nitrogen data provide insight to the elemental processes occurring during thermal degradation at different fuel moistures.

## **2.4 Statistical Analysis**

A bivariate Pearson correlation was used to test the relationships between the active fire measurement of FRE and the post-fire variables of (1) pyrC, (2) BC, and (3) BC:pyrC ratios. Correlation was also used to test the relationship of the BC:pyrC ratio and the C:N ratio. Both FRP 95<sup>th</sup> percentiles and FRE comparisons between the 4-8% and 13-15% moisture groups were conducted using t-tests. One-way 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 BC concentrations, (3) pyrC production, (4) BC production, (5) the BC:pyrC ratio, (6) pyrC and BC isotopes, and (7) pyrC:N and BC:BN ratios. All statistical analysis was conducted using IBM SPSS predictive analytics software, version 19.

## **3. Results and Discussion**

### **3.1 Fire Characteristics**

Flame heights decreased from 30 cm in the driest fuels to 12 cm in the 13-16% fuel moisture group, visually indicating a difference in fire behavior between the fuel moisture groups (Table 1.2). Furthermore, duration of flaming combustion was shorter in the 4-8% (6 min 54 sec) and 10-12% (10 min 02 sec) relative to the 13-16% moisture group (14 min 44 sec). FRP data corroborate the flaming combustion results, and show much higher peak radiant flux values in the 4-8% moisture group compared to the 13-16% moisture group (Figure 1.2). Time-integrated FRE data illustrate that despite prolonged flaming duration in

the 13-16% moisture group, this moisture group tended to burn with much less overall intensity than the two drier fuel moisture groups (Figure 1.2). It is important to note that the sensitivity of the sensor to record low radiant heat signals led to a difference in total number of observed FRP data points. Given that the sensor did not record as many FRP points in the 13-16% fuel moisture trials, the fire temperatures in this fuel moisture group were likely much lower than fuels burnt at 4-8%.

Peak FRP flux recordings occurred when the fuel bed was entirely engaged in flaming combustion. Differences in peak FRP flux times were apparent between the two moisture groups, with the dry fuels producing peak FRP values around 500-600 seconds after ignition, and the wet fuels peaking at approximately 1000-1100 seconds after ignition (Figure 1.2). While smoldering combustion times were highly variable and yielded no significant results, radiant heat release dropped below the detection limit in the 4-8% fuel moisture group at 2000 seconds, and close to 2500 seconds in the 13-16% moisture group, indicating sustained low intensity smoldering combustion in the 13-16% fuel moistures. The differences in radiant flux values between wet and dry fuels correspond well with surface soil temperature data measured using thermocouples in masticated fuels evaluating lethal soil temperatures, which indicate peak soil temperatures of 500-600°C occurring early in the burn when fuel moistures were near 2%, and peak temperatures of 400-500°C occurring later in the burn when fuel moistures were 16% [Busse *et al.*, 2005].

### **3.2 Carbon Concentrations**

Carbon concentrations for pyrC ranged from 15.37 to 74.45%, with the < 1mm particles displaying the lowest pyrC concentrations, and the > 6mm particles containing the highest concentration (Table 1.3). The lack of pyrC in the < 1mm size class may be a

function of the high ash content in this size class [Nocentini *et al.*, 2010]. Trends across fuel moisture, regardless of residue size, show a slight increase between 4-8% and 10-12%, with the least amount of pyrC being contained in the 13-16% moisture group. In contrast, BC concentrations were the greatest in the 13-16% moisture group (ranging from 0.49 to 2.65%), regardless of residue size. Although the 13-16% moisture groups contained the smallest pyrC concentrations, a greater percentage of the residue was converted to BC. Also, in the 13-16% fuel moisture the concentration was an order of magnitude greater > 6mm size class. This trend was only observed in the wettest fuel moisture group, the drier moisture groups maintained similar concentration amounts regardless of size class.

### 3.3 Post-fire Residues

Total fuel bed consumption did not vary as a function of fuel moisture (Table 1.4). Once fire had established in the masticated fuel beds it sustained the combustion reaction until nearly 90% of the fuel bed was consumed. Weight of the total post-fire residues, and residues by size class also did not vary as a function of fuel moisture (Figure 1.3a). Dry biomass conversion to post-fire charred residues and ash averages were 9.60 (2.73)%, 8.78 (1.95)%, and 10.22 (3.38)% for the 4-8%, 10-12%, and 13-16% fuel moisture ranges, respectively. Despite sampling differences and fire behavior, these values are very similar to conversion rates of 8.0% measured volumetrically by *Tinker and Knight* [2001], who only measured charred residues in coarse woody debris in Yellowstone National Park. Other studies measuring charcoal production via gravimetric and volumetric means are difficult to compare to, as they tend to use approximate carbon values for the post-fire residues [Fearnside *et al.*, 1999; Forbes *et al.*, 2006]. Although total fuel bed consumption did not significantly differ in our statistical analysis as a function of fuel moisture, the average post-

fire residue weight in the 13-16% fuel moisture group was slightly higher than the average weight of the two dryer fuel moisture groups. Within the post-fire residues, the majority of the residue was allocated in the < 1mm and > 6mm size classes, perhaps indicating that the majority of the pine needles were either volatilized or fragmented to <1mm in size. The 4-8% and 10-12% fuel moistures contained the majority of their mass in the <1mm size, while the 13-16% fuel moistures contained the largest amounts of post-fire mass in the >6mm size class. These results suggest that at higher fuel moistures the masticated woody particles only partially combusted and did not fully consume or fragment to smaller sizes, unlike masticated fuels burnt under drier conditions.

### **3.4 Pyrogenic Carbon Production**

PyrC production in the post-fire residues averaged 200.63 to 252.32 g m<sup>-2</sup>. Although there were no significant differences between fuel moisture groups, pyrC content generally increased with fuel moisture, which is a function of the slightly higher residue weight (Figure 1.3b). Conversion rates of the pyrC relative to pre-fire OC range from 7.23 to 8.54% (Table 1.4). When rates are normalized by total pre-fire dry weight, pyrC production ranges from 3.52 to 4.22% (data not shown), which compare well with conversion rates of 4.8% observed in a slash and burn study in a temperate deciduous forest, utilizing elemental analysis of the post-fire residues [Eckmeier *et al.*, 2007]. Similar to the slash and burn fuel type measured in Eckmeier [2007], masticated fuel beds in the present study also contained a large proportion of small diameter woody materials. Production rates are slightly higher than those observed in South American rain forests of 1-3%, which is likely a function of the large woody component in the masticated fuels [Fearnside *et al.*, 2001; Fearnside *et al.*, 1999]

Similar to the trends in concentration, most of the pyrC produced was allocated in the > 6mm size class charred particles, while the least amount of pyrC located in the < 1mm residues. Pyrogenic carbon slightly decreased in the small size fraction with increased fuel moisture, but increased with fuel moisture in both the 1-6mm and >6mm size fractions. Finally, correlation analysis between pyrC production and FRE was not significant,  $R = 0.008$  ( $p = 0.985$ ,  $n = 10$ ).

### 3.5 Black Carbon Production

Similar to the pyrC production, total BC production increased from 0.02% to 0.05% between the 13-16% moisture group and the two drier fuel moisture groups (Table 1.4). This increase in BC production as a function of fuel moisture was observed in all size classes, though the medium-size residues showed no change between the 10-12% and 13-15% (Figure 1.3c). In contrast to the pyrC results, the majority of BC was allocated in the fine (< 1mm) size fraction (ranging from 0.27 to 0.90 g m<sup>-2</sup> for the 4-8% and 13-15% fuel moisture groups, respectively), suggesting that at least some of this material was likely BC formed through the recondensation of volatiles, and highly resistant to our methods of thermal and chemical degradation. These results also appear contrary to *Nocentini et al.* [2010] who suggest that the coarsest size fraction contains the largest amount of highly aromatic structures. However, their elemental analysis was limited to what this study defining as pyrC, and they did not quantify BC as this study does. Additionally, *Nocentini et al.*[2010] limited their largest size class to >2mm, which we included in our middle size class. The coarse charred material, while high in pyrC, contained the least amount of BC (from 0.002 to 0.007 g m<sup>-2</sup>). These results suggest the possibility that the fire temperature required to convert the

organic carbon to BC did not achieve high enough temperatures for conversion towards the interior of the macro-size woody particles.

These results appear somewhat counter-intuitive compared to other studies which find that BC production increases with fire severity in pine needles [Hatten and Zabowski, 2009]. In the present study, FRE was strongly negatively correlated with BC production,  $R = -0.845$  ( $p = 0.004$ ,  $n = 10$ ), suggesting that at high overall fire intensities less BC was produced. These results suggest that under lower fuel moisture levels (e.g. increased fire intensities) BC is preferentially volatilized, as overall fuel bed consumption did not vary.

### **3.6 Black Carbon to Pyrogenic Carbon Ratio**

The ratio of black carbon to pyrogenic carbon reflects the relative degree of resistance to biological degradation in the fire-altered residue [Hatten and Zabowski, 2009]. Similar to the pyrogenic and BC production, the ratio for the total fuel bed increased with fuel moisture, indicating a greater resistance to chemical and thermal degradation at higher fuel moistures (Figure 1.3d). FRE was also negatively correlated with the BC:pyrC ratio  $R = -0.695$  ( $p = 0.038$ ,  $n = 10$ ), again suggesting that fuels burnt at low fuel moistures the fire will volatilize the majority of the pre-cursors to black carbon. Similar to BC production, the highest ratio was observed in the fine (< 1mm) sized particles (ranging from 0.007 to 0.03 for 10-12% and 13-16% moisture groups, respectively). These results suggest that that the majority of BC created in masticated fuels exist in the > 1mm size class. The < 1mm size class represented the majority of the post-fire residues regardless of moisture. It also maintained the highest BC:pyrC ratio, suggesting that this size class is important in the formation of BC in masticated fuels. The smallest BC:pyrC ratios were observed the coarse (>6mm) size

residues, indicating that while large quantities of pyrC are created in this size class, most of it will be subjected to future degradation.

### 3.7 Composition of Fire Altered Organic Residues

The largest pyrC:N ratio was observed in the >6mm size class, with smaller ratios in the two smaller size classes (Table 1.5). These trends are similar to the unburnt fuel C:N ratios, suggesting that fragmentation of the woody particles was not a significant contributor to pyrC:N ratios. If even a small amount of the fuel particles were fragmented from a larger size class (e.g. > 6mm) size fraction to one of the other smaller size fractions (e.g. 1 - 6mm) there would have likely 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  $\delta^{13}$  pyrC isotope data, and variation in the isotope data is likely due to variability in the parent material.

Regardless of size class, pyrC:N ratios were less than unburnt C:N ratios, indicating that regardless of fuel moisture, C was preferentially volatilized relative to N (Table 1.5). 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 > 6mm and < 1mm size classes, where lower C:N ratios were found at higher fuel moistures. Our data support the concept that the presence of N in organic matter is important in the production of highly recalcitrant black carbon. Previous work has suggested that nitrogen provides stability to chars at temperatures under 450°C, and C:N ratios increase with temperatures above this threshold [Knicker, 2010; Knicker *et al.*, 2008]. 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 of the organic residue than would be expected for a residue with a high C:N.

The stable isotopic composition of the <6mm fractions was lighter than the unburned material suggesting that lignin (typically ~3 ‰ lighter than cellulose) was preferentially preserved or transformed into pyrC. The slightly heavier, yet statistically significant, stable isotopic composition of the < 1mm fraction burnt at the highest fuel moisture suggests that more carbon from cellulose was preserved relative to the higher intensity treatments. We hypothesize that heavier isotopic composition and lower C:N ratios was a result of N thermally stabilizing pyrC at this higher fuel moisture and low burn intensity. A possible mechanism could be that products of cellulose pyrolysis (i.e. depolymerization and release of anhydro sugars) reacted with N containing compounds in the Maillard reaction forming thermally stable compounds such as pyridinies, pyrazines, and pyrroles.

At low fuel moistures it appears that more indiscriminate combustion of all compounds occurred, as C:N ratios trended closer towards unburned materials. A Pearson correlation analysis between the BC:pyrC ratio and C:N ratio, produced a moderate negative correlation of  $R = -0.602$ , ( $p = < 0.001$ ,  $n = 15$ ), supporting the idea that the presence of N is important in producing high BC:pyrC ratios.

BC to black nitrogen ratios are much lower than pyrC:N ratios, further supporting the concept that N plays a strong role in thermal stabilization of C [Knicker, 2010]. Since more N may be available to react and form BC, the selective preservation of N in the higher fuel moisture may be causing the increased rates of BC production in the 13-16% fuel moisture group. BC  $\delta^{13}\text{C}$  data in the > 6mm size class again support the theory that indiscriminate

combustion is occurring at lower fuel moistures, as lignin and cellulose are preferentially being removed at higher fuel moistures.

#### **4. Conclusions**

The production of BC and elemental composition of our post-fire residues varied as a function of fuel moisture, with highest BC production rates and BC:pyrC ratios in residues burned at 13-16% fuel moisture. Correlations between FRE and BC and FRE and BC:pyrC yielded significant results indicating that fire intensity a key contributor to BC production and/or BC volatilization, where in dry fuels pre-cursors to BC were indiscriminately consumed at high radiant intensities early on in the combustion process. Fuels burnt at higher fuel moistures tended to preserve these precursors for the eventual conversion to BC. The threshold fuel moisture between BC production and volatilization in our masticated fuel beds occurred between 12-13%.

Fuel moisture is an easily measurable variable and often dictates fire management decisions, especially in prescribed fires. Based on the present study, management strategies that emphasize carbon retention should consider burning when fuel moistures are greater than 12% if possible, to maximize the BC conversion and minimize volatilization. With low production rates of 0.02 to 0.05% (relative to pre-fire OC), BC is likely not an important contributor to stand-level soil carbon in the short term (e.g. one fire event). Over time, and multiple fire events, BC may slowly increase a stand's long-term carbon pool if it can be sufficiently insulated from degradation mechanisms. However, it remains unclear whether or not multiple fire events create more BC, or reduce BC levels through the burning of unprotected BC [Rovira *et al.*, 2009].

The experimental approach used in this study allowed for a unique opportunity to control and replicate burns under fixed fuel moistures. The utilization of the dual-band thermal infrared sensor allowed for accurate characterization of radiant heat release throughout the entire burn period. This sensor, or similar sensors, should be considered for future studies evaluating fire behavior and subsequent effects in conjunction with thermocouples for correlation between fire temperature and FRE, as these “remotely sensed” data may be scaled up to stand and landscape-level prescribed fires and wildfires. Future BC production studies should attempt to accurately characterize both the pre-fire fuel characteristics as well as fire behavior, as both have been shown to play a critical role in determining the post-fire composition of the residues. Moreover, studies evaluating the persistence of fire-altered carbon should include both experimental combustion studies as well as field studies in a broad range of fuel types, as well as field validation of our results.

More research is clearly warranted to determine if fuel moisture has a similar effect on BC production on masticated fuels in the field, or if other environmental factors controlling fire behavior (e.g. wind speed) have a greater impact on BC production. This is especially needed in stands managed for multiple objectives where 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 into predicted fire behavior, including duration of smoldering combustion beneath the surface, within such masticated fuel beds. Improved understanding is needed to characterize the behavior and effects under varying bulk densities and wind speeds. As noted earlier, very little research has been conducted in wildfire and prescribed fires to test how specific fuel properties and weather characteristics influence fire behavior and subsequent production of BC. 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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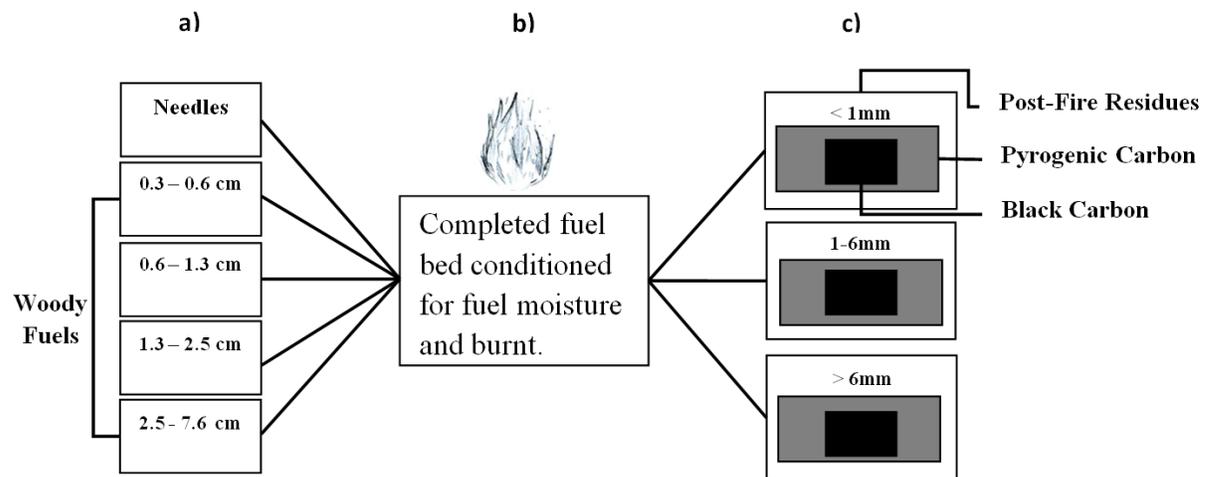
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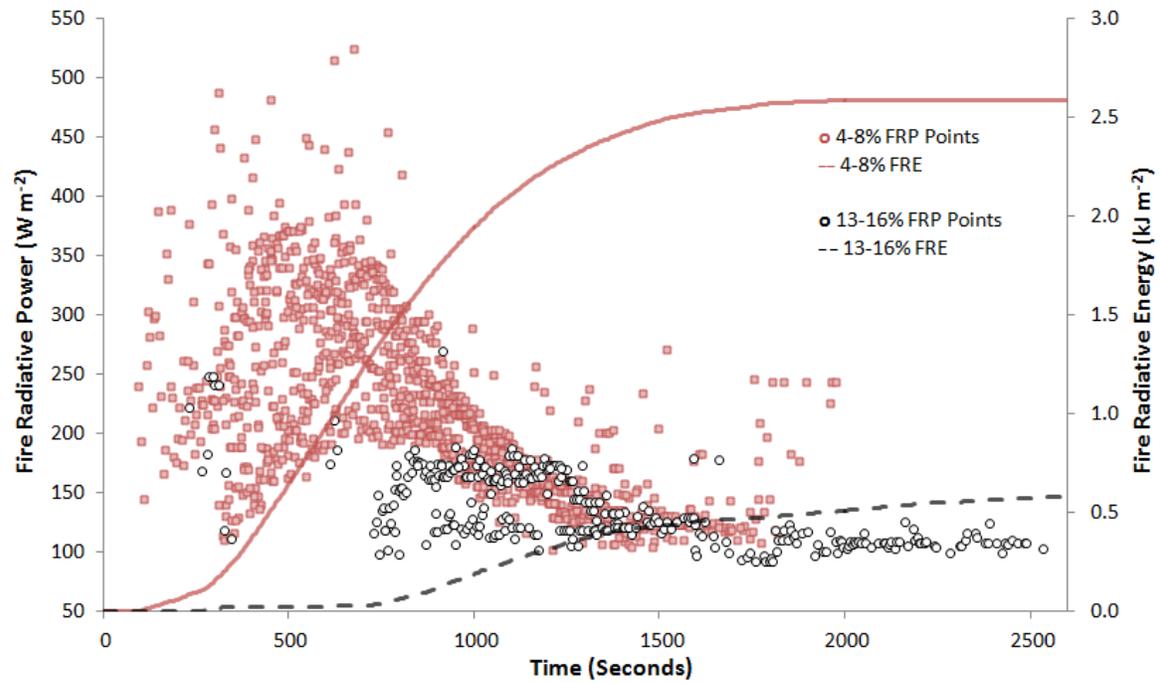
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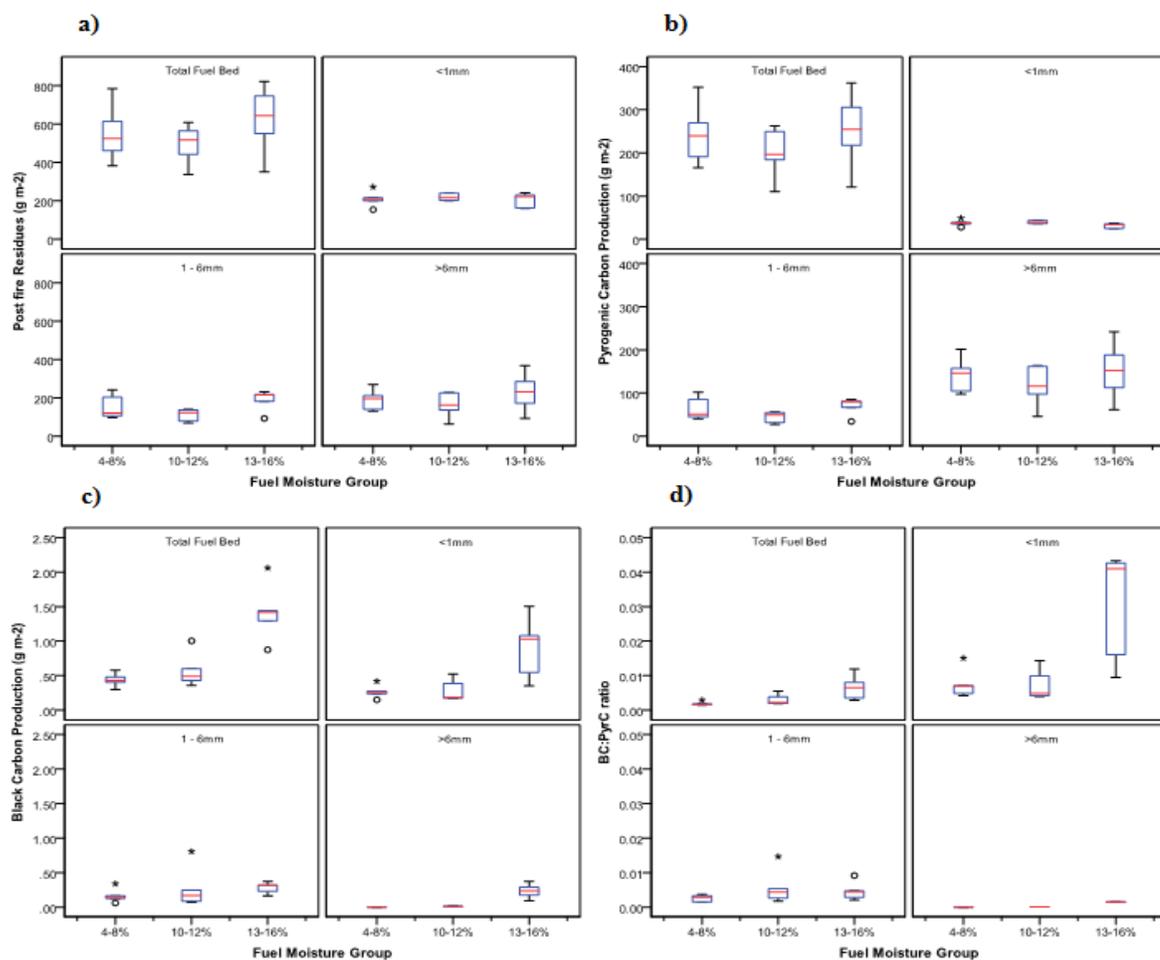
**Figures:**



**Figure 1.1:** Flow chart showing (a) fuel bed composition, (b) the completed fuel bed, and (c) post-fire residue size classes and carbon components.



**Figure 1.2:** Fire radiative power flux points ( $n = 5$  for each fuel moisture group) corresponding with the primary y-axis. Average integrated fire radiative energy (FRE) values are shown with lines, and correspond with the secondary y-axis.



**Figure 1.3:** Post fire components by moisture group and size class, (a) residue weight, (b) pyrC production, (c) BC production, and (d) The BC to pyrC ratio. Outlier values  $>1$  and  $>2$  standard deviations away from the mean are shown by \* and  $^{\circ}$  respectively.

## Tables

**Table 1.1:** Mean (SD) fuel bed characteristics and ambient burn conditions for each fuel moisture category (n=5 for each moisture category).

<b>Moisture Group</b>	<b>Dry Weight (g m<sup>-2</sup>)</b>	<b>Organic Carbon (g m<sup>-2</sup>)</b>	<b>Bulk Density (Kg/m<sup>-3</sup>)</b>	<b>Temperature (°C)</b>	<b>Relative Humidity (%)</b>
4-8%	5668.26 (148.44)	2739.75 (71.75)	105.45(13.40)	21.05(1.83)	32.34(7.81)
10-12%	5764.78 (106.26)	2786.41 (51.36)	96.46(2.88)	19.63(7.02)	38.48(14.41)
13-16%	5932.45 (184.50)	2815.79 (89.18)	104.25(7.35)	22.76(2.55)	34.39(8.18)

**Table 1.2:** Fire characteristics by moisture levels ( $n = 5$ ). Homogenous subsets identified by a, b, c ( $\alpha = 0.05$ ).

Moisture Group	Average Integrated FRE (kJ m <sup>-2</sup> )	Radiant Flux (W m <sup>-2</sup> )	FRE 95th percentile	Flame Height (cm)	Flame time (min:sec)	Smolder time (hr:min:sec)
4-8%	0.26 (0.07) a	220.87 (76.38) a	339.27 (19.99) a	30.00 (6.00) a	6:54 (1:20) a	2:40:02 (1:06:53)
10-12%	-	-	-	23.00 (4.00) a	10:02 (2:30) a	2:11:04 (1:31:14)
13-16%	0.05 (0.04) b	137.90 (31.03) b	160.17 (18.29) b	12.00 (4.00) b	14:44 (3:03) b	3:03:00 (46:38)
<i>p-value</i>	<i>&lt;0.001</i>	<i>0.001</i>	<i>0.001</i>	<i>0.001</i>	<i>0.001</i>	<i>0.525</i>

**Table 1.3:** Mean (SD) pyrC and BC concentrations (%) for each fuel moisture groups.

ANOVA comparisons were analyzed across moisture groups (n = 3 for pyrC, and n = 5 for BC). Homogenous subsets from Tukeys post-hoc analysis identified by: a, b, c ( $\alpha = 0.05$ ).

<b>Material Type</b>	<b>Moisture Group</b>	<b>&lt;1mm</b>	<b>1-6mm</b>	<b>&gt;6mm</b>
PyrC Concentration	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-value:</i>		<i>0.495</i>	<i>0.708</i>	<i>0.021</i>
BC Concentration	4-8%	0.14 (.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-value:</i>		<i>0.006</i>	<i>0.654</i>	<i>&lt;0.001</i>

**Table 1.4:** Mean (SD) for post-fire residues, pyrC, BC, and the BC:pyrC ratio for each size class of post-fire material, as well as the total combined fuel bed. ANOVA was used to analyze differences across moisture levels. Homogenous subsets are indicated by: a, b, c as tested by Tukeys post-hoc test ( $\alpha = 0.05$ ).

Material Type	Moisture Group	< 1mm	1-6 mm	> 6mm	Total Fuel Bed	Consumption (%)	Production (%)
Post-fire residues (g m <sup>-2</sup> )	4-8%	210.06(42.23)	154.00(64.80)	189.74(56.75)	571.65(155.93)	90.39(2.73)	9.60(2.73)
	10-12%	220.98(19.72)	109.56(33.14)	163.30(68.43)	493.84(107.34)	91.31(1.85)	8.78(1.95)
	13-16%	203.68(38.21)	188.42(56.29)	230.37(105.51)	622.47(183.94)	89.71(2.93)	10.22(3.38)
<i>p-value</i>		0.735	0.103	0.433	0.904	0.622	0.623
Pyr C Production (g m <sup>-2</sup> )	4-8%	39.65(3.54)	43.96(13.3)	117.02(49.04)	200.63(60.64)	91.33(2.73)	8.67(2.63)
	10-12%	37.7(7.58)	64.72(27.23)	141.26(42.26)	243.68(72.81)	92.77(2.13)	7.23(2.13)
	13-16%	31.31(5.87)	69.58(20.79)	151.42(69.35)	252.32(91.4)	91.46(3.00)	8.54(3.00)
<i>p-value</i>		0.105	0.171	0.607	0.533	0.667	0.638
BC Production (g m <sup>-2</sup> )	4-8%	0.27(0.10) a	0.17(0.10)	1.73E-03(5.18E-04) a	0.44(0.10) a	100(0.00) a	0.02(0.00) a
	10-12%	0.29(0.16) a	0.28(0.30)	1.07E-02(4.47E-03) a	0.58(0.25) a	100(0.00) a	0.02(0.01) a
	13-16%	0.9(0.46) b	0.28(0.08)	2.34E-01(1.07E-01) b	1.42(0.42) b	99.99(0.00) b	0.05(0.01) b
<i>p-value</i>		0.006	0.580	<0.001	<0.001	<0.001	<0.000
BC:pyrC	4-8%	7.65E-03(4.33E-03) a	2.59E-03(1.03E-03)	1.23E-05(2.07E-21) a	1.88E-03(5.80E-04) a	-	-
	10-12%	7.48E-03(4.57E-03) a	5.80E-03(5.16E-03)	9.12E-05(1.66E-20) b	4.31E-03(2.54E-03) a, b	-	-
	13-16%	3.05E-02(1.64E-02) b	4.66E-03(2.76E-03)	1.54E-03(1.57E-21) c	6.59E-03(3.65E-03) b	-	-
<i>p-value</i>		0.005	0.356	<0.001	0.019	-	-

**Table 1.5:** Mean (SD) C:N and  $\delta^{13}\text{C}$  VPDB x 1000 isotope values for pyrC and BC by residue size (n = 3 for pyrC, n = 5 for BC).

Unfortunately too little sample remained to gather standard deviations for values of BC > 6mm. ANOVA was used to test for differences across moisture level, homogenous subsets are identified by: a, b, c from Tukeys post-hoc analysis ( $\alpha = 0.05$ ).

Residue Type	Moisture Group	C:N			$\delta^{13}\text{C}$ Isotope (‰)		
		<1mm	1-6mm	>6mm	<1mm	1-6mm	>6mm
Unburnt Carbon	na	na	103.13(16.21) <sup>†</sup>	477.64(52.37) <sup>†</sup>	na	-26.74(0.11)*	-27.16(0.09) <sup>†</sup>
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>p-value</i>		<0.001	0.611	0.001	0.023	0.948	0.214
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>p-value</i>		0.086	0.805	-	0.013	0.184	-

<sup>†</sup> In unburnt fuels, this size class represents the pine needle component

<sup>‡</sup> The >6mm size class unburnt particles are woody

## Chapter 2

### Quantifying the Response of Fire-Altered Residue to Repeated Burning

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**Abstract:**

Black carbon (C) in post-fire residues is the byproduct of incomplete combustion from biomass burning, and provides an avenue in which labile organic C is transferred into passive carbon pools. Given historic fire frequencies and black carbon production rates, observational studies have found soil black C to be much less than anticipated, indicating the important role of post-fire degradation of black C. Several mechanisms degrade black C once it has been created through biomass burning. One poorly understood mechanism is loss through repeated burn events, which may be a primary mechanism of black C loss in high fire frequency ecosystems. Here we present loss rates of macro-charcoal particles (> 6mm) and their pyrogenic C and black C portions through four repeated burn events, using fifteen experimental fuel beds for a total of 75 burn trials. We show that after the initial generation of the black C in the first fire event, loss rates are 39, 79, 98, and 99% for burns 2 – 5, respectively. Using these loss rates as parameters we construct a model to predict net black C stocks through five fire events. Comparing our budget to a simple mass balance equation with no losses, we observe an 88% difference between the two scenarios in the black carbon produced and lost after 5 fires.

## 2. Introduction

Future climate scenarios will likely cause an increase in fire activity in the Western U.S. and may lead to unprecedented impacts of forest carbon stocks [Westerling *et al.*, 2006]. Recent studies have highlighted the importance of black C in forest carbon cycling, as this highly resistant thermally altered biomass may be stored in passive soil carbon pools if successfully integrated into the soil matrix [DeLuca and Aplet, 2008; Ohlson and Tryterud, 2000]. Black C has the potential to provide an avenue for fire-affected ecosystems to slowly increase their sink capacity over several fire events, which will become increasingly important given the predicted increased fire frequencies throughout many temperate forest types [Czimczik and Masiello, 2007; Flannigan *et al.*, 2009].

The fire environment under which the black C forms likely controls the long-term stability of the fire-altered organic matter [Keiluweit *et al.*, 2010]. Fire-altered material produced around 300-400°C are more resistant to biologic degradation than residues formed at lower temperatures [Bruun *et al.*, 2008; Nguyen *et al.*, 2010]. However, at higher fire intensities the majority of black carbon may be volatilized leaving less black C to be mixed into soil horizons. Increased resistance is due to the changes in atomic structure, principally reductions in the H:C and O:C ratio as charring intensity increases [Kuhlbusch *et al.*, 1996]. The degree of charring (or temperature and duration) has also been shown to control the resistance to chemical oxidation, and soil mineralization rates [Bruun *et al.*, 2008; Hockaday *et al.*, 2006]. In wildfire and prescribed fire events the degree of charring is not easily measureable due to the dynamic and highly variable fuel arrangement and subsequent fire behavior. To fully understand the mechanisms associated with black C degradation, it is first

important to accurately characterize fuel conditions and arrangement, and subsequent fire behavior ([*Czimczik et al.*, 2003; *González-Pérez et al.*, 2004]).

Several mechanisms influence the fate and deposition of newly created black C [*Czimczik and Masiello*, 2007; *Preston and Schmidt*, 2006]. Erosion processes can horizontally transport 7-55% of the pyrogenic carbon offsite where it may be stored in lake beds and marine environments [*Rumpel et al.*, 2009; *Schmidt*, 2004]. Other physical processes such as freeze-thaw events, bioturbation, and wind throw aide in integrating black carbon into the mineral soil horizon, to become a part of the passive carbon pools [*Gavin*, 2003]. In addition to the physical processes which transport recently created black C to passive pools, biodegradation mechanisms act upon the black carbon particles after conversion [*Baldock and Smernik*, 2002; *Bruun et al.*, 2008].

Fire frequency exhibits a somewhat paradoxical relationship with black C [*DeLuca and Aplet*, 2008; *Rovira et al.*, 2009]. On the one hand black C is continually generated and accumulated in pyrogenic ecosystems that experience high frequency fires which lead to increased soil black C over time [*Czimczik and Masiello*, 2007; *Czimczik et al.*, 2003]. On the other hand, subsequent fires may actually volatilize the black C from a previous fire before it can be successfully incorporated into the passive carbon pool [*Ohlson and Tryterud*, 2000; *Rovira et al.*, 2009]. In temperate forests, soil incorporation and offsite transport rates likely determine the how much black C available to be burnt in repeated fires. Although belowground fire consumption can occur in some ecosystems in the first 5-10cm (e.g. boreal forests), at soil depths > 1mm, charred residues are likely to be insulated from the effects of subsequent burning as temperatures required for thermal degradation cannot be achieved [*Humphreys and Craig*, 1981]. The time required for charred particles to reach insulation

depth is has yet to be determined. One year following a fire, only small increases in soil organic carbon concentrations were observed from 0-1 cm; which suggests that full incorporation of the post-fire residues likely occurs on decadal or century time scales, which is much longer than mean fire return intervals in many forest types [Eckmeier *et al.*, 2007a]. Uncertainly exists on whether black carbon produced in a fire will be stored or remain available for combustion in a subsequent fire; especially in forests that experience short fire return intervals [Rovira *et al.*, 2009].

Mass balance estimates of black C have greatly overestimated black carbon in soils given historic fire frequencies, indicating that degradation of black C occurs from various mechanisms [Ohlson and Tryterud, 2000]. Soil C models which assume no black C mineralization have been shown to overestimate black C over time when black C “disappearance” is included [Lehmann *et al.*, 2008]. To better calculate additions to the passive soil-C pool, it is therefore critical to identify black C degradation mechanisms and quantify rates of black C loss, including repeated burning. The objectives of this study are: 1) to characterize the loss rates of macro-charcoal particle weight (>6 mm), pyrogenic C, and black C as a function of four repeated burn events, simulating a high fire frequency regime where all of the residues from the previous fire are available to be burnt again and 2) quantify changes in elemental composition of the residues as a function of repeated burning to better understand how repeated burning affects organic matter composition and 3) incorporating the loss rates characterized in the macro-charcoal particles, we reconstruct a black carbon budget over five burn events and discuss the differences between mass balance equations and models which include black C loss [Lehmann *et al.*, 2008]. It is important to note that although these loss rates inform the thermal degradation of pyrogenic residues through

repeated burning, 90% of the biomass loss occurs in the initial fire where biomass is converted from pre-fire organic material to post-fire residues, pyrogenic C, and black C. As black C represents a potential pathway to long-term C stabilization (mean residence times of ca. 1-10k), it is therefore to quantify its loss rates that are associated with repeated burning.

## 2. Methods

The construction of the initial masticated fuel bed was achieved by first collecting material from 20 quadrat-plots within an 8 ha masticated stand on the Clearwater National Forest, Idaho (Latitude 46.801 N, Longitude 119.47 W). For full details on the sample collection and fuel bed construction methodology, refer to Brewer et al. (in review). To characterize the typical masticated fuel loading and particle size mix, the material from each quadrat was individually sorted into five different size classes (7.6 - 2.5 cm, 2.5 - 1.3 cm, 1.3 - 0.6 cm, and 0.6 - 0.3 cm, and needles), dried at 100°C until weights remained constant, and weighed. Additional masticated material was also collected from the site, and fifteen fuel beds were then constructed using estimates of average dry weights of each particle size class.

In addition to the 15 masticated fuel beds used for the initial burn, sixty pine needle fuel beds were assembled for the repeated burns, comprised of a 50/50% mixture of lodgepole pine (*Pinus contorta*) and Ponderosa pine (*Pinus ponderosa*) needles. The needle fuel beds were constructed to resemble fuel loading and bulk density conditions commonly observed in temperate forests found throughout Western U.S. and Canada (Table 2.1)[Brown, 1981]. The remaining residues (> 6 mm) from the original 15 fuel beds were then reincorporated into pine needle matrix and burnt simulating a repeated fire event. In naturally occurring fuel beds charred particles will likely reside near the bottom of the litter and duff horizons, and by mixing we likely overestimated the losses associated with repeated burning.

Fuel moistures ranged from 2.8 to 18.5%, thus capturing fuel moisture conditions that exist in the field during wildfires and prescribed fires (Table 2.1). Macro-charcoal (>6mm) particles from each of the 15 fuel beds were burnt a total of four times following the initial fire, for a total of 60 trials. Residues smaller than 6mm were not carried forward as they were indistinguishable from the newly burnt pine needles.

Seventy five total burn trials were conducted at the Idaho Fire Laboratory. Fuels were placed on the table and a small strip of lighter fluid was placed on the leading edge of the burn and ignited. Burns were considered completed when mass was no longer lost, measured with a Sartorius EB Series scale (Goettingen, Germany), inserted into the burn platform below the fuel bed.

Following burning, post-fire residues were sieved into > 6mm, 1-6mm, and < 1mm size classes and a two ~1g subsamples were analyzed for 1) pyrogenic C and 2) black C. Pyrogenic C refers to the total amount of C present in the post-fire residues, identified by elemental analysis. Black C was quantified using thermo-chemical methods adapted from CTO375 protocols, which isolates the biologically resistant portion of the pyrogenic C [Gustafsson *et al.*, 1997; Hatten and Zabowski, 2009].

A repeated measures ANOVA was used to test for differences in post-fire charred material, pyrogenic C, and black C for each burn trial. When Mauchly's sphericity assumption was not met, the Greenhouse-Geisser statistic was used, which does not assume sphericity. A Bonferroni post-hoc test was used to compare the main effect of burn number. Loss rates through five fires were modeled using exponential regression, with the equation:  $y = e^{(-kt)}$ . Statistical analysis was conducted using IBM SPSS predictive analytics software, version 19.

### 3. Results and Discussion

Residue weight, pyrogenic C, and black C all exhibited highly significant losses through the five fires ( $p = <0.001$ ), however maximum loss rates between the three variables occurred between different fires (Figure 2.1). Our loss rates through two repeated burns, 79%, are much higher than results in a Mediterranean shrub ecosystem of 41% [Rovira *et al.*, 2009]. However, our loss rates do not include the production of new black carbon from the pine needle fuel bed, which will likely offset a portion our calculated loss rate. Loss in residue weight primarily controlled the loss in pyrogenic carbon. The maximum period of loss for both residue weight and pyrogenic carbon occurred during the second fire, i.e. first repeated burn, where only 56% of the residues and pyrogenic carbon following the fire event (Table 2.2). Following four repeated burns only 19.46% of the post-fire residues remained, while only 5.94% of the pyrogenic carbon remained.

Residue mass loss was also important in determining black carbon loss rates, especially in the first three fires. However, unlike the residues and pyrogenic carbon, black carbon experienced its greatest rate of loss at burn three, where only 20.45% remained after the third fire. Through the fifth repeated burn only 1.06% of the black carbon created in the initial fire remained, suggesting the preferential removal of black carbon through repeated burning relative to residue mass loss and pyrogenic carbon loss. Moreover, these loss rates suggest that in high fire frequency regimes, black carbon from a singular fire event can be nearly entirely depleted after 4 repeated burns, leading to less black carbon available to be incorporated into the passive soil carbon pool, thus possibly helping explain why forest soils much more black carbon-deficient than expected given historic fire regimes and black carbon production rates [Ohlson and Tryterud, 2000].

The ratio of black C to pyrogenic C, used as a proxy to determine the recalcitrance of the fire-altered carbon also declined through the five burn events (Figure 2.2). Similar to black C, the greatest loss occurred between burns 2 and 3. These trends suggest that over multiple fire events, the original black C created from the first burn is becomes less stable as a function of repeated burns and it is likely available for rapid mineralization. The inclusion of O:C and H:C ratios would have been helpful in testing the relative recalcitrance of the charred residues, and future studies evaluating repeated burning should include these ratios [Kuhlbusch *et al.*, 1996].

### **3.1 Elemental Composition and Isotope changes**

Despite there being no significant differences in pyrogenic concentration through the five fire events, there was a slight depletion in pyrogenic C concentration that occurred after the fourth and fifth repeated burn (Table 2.3). These small differences in pyrogenic C concentrations in combination with residue mass loss led to large differences in remaining residues, pyrogenic C. Nitrogen (%) values increased slightly through the first four fires, from 0.34 to 0.49%, but then returned to 0.35% following the fifth burn (data not shown). Pyrogenic C:N levels were quite variable, but generally decreased as a function of repeated burns, suggesting both C loss and N enrichment were occurring in the fire events. The presence of N in thermally altered residues plays an important role in C stabilization and the creation of highly biologically resistant pyrogenic C [Knicker, 2010]. However, the mass of the charred residue continued to be reduced through the repeated burns, leading to almost 95% pyrogenic C loss and > 99% black C loss. In high fire frequency forests, biologic degradation of the fire-altered residues may not be as important as C losses through repeated burning.

Similar to pyrogenic carbon, black C, showed a general decline in concentrations through the five burns (table 2.3). Black nitrogen concentrations remained relatively consistent throughout the five burns ranging from 0.11 to 0.14%, with no identifiable trend of increase or decrease (data not shown). Burn 2 black C concentrations controlled black C:N ratio were greatest at  $1.06 \pm 0.14$  %, which led to the highest BC:BN ratio, and burn 4 produced the smallest BC:BN ratio. The black C and N concentrations parallel the pyrogenic carbon and nitrogen data, with burn two producing the highest pyrogenic C and black C concentrations, and burn four producing the lowest concentration levels. Following thermal oxidation and HCl treatment,  $\delta^{13}$  isotope values were generally greater than pyrogenic  $\delta^{13}$  isotope values, but isotopic signatures were similar throughout the five fires. Furthermore,  $\delta^{15}$  N isotopic signatures were enriched throughout repeated burning from  $2.10 \pm 2.00$  at the first burn to  $5.78 \pm 1.03$  following the fifth burn.

### **3.2 Modeled Carbon Budget**

Using the loss rates for the > 6mm charred particles; we conducted an exercise in which we calculated carbon gains (through a production term) and losses over 5 burn events for net black C (e.g. “with loss”). In each fire event fire-altered carbon was produced. However, after the initial fire some proportion of the existing fire-altered material lost in secondary fires. For the purposes of this budget we assume the rate of loss for the entire fuel bed is consistent with the loss rate associated with the > 6mm charred particles. Future studies evaluating net black C production should seek to improve upon this idea that all post-fire residues are lost at the same rate, regardless of size class. However, in this initial attempt we will assume loss rates are constant across all sizes of post-fire residues. For the “no loss” scenario, the amount of post-fire residue, pyrogenic C, and black C produced in the fire event

was simply added to the pre-existing amounts. When loss rates were included, the production amount from the previous fuel bed was multiplied by the appropriate loss rate, subtracted out, and the remaining amount was added to the production of the most recent fire (Figure 2.3).

Trends for “no-loss” scenarios were linear, showing constant gain (or production) after each fire event, while net trends (those including loss rates) show much less black C over 5 fires. Comparing net production between the “no-loss” and “loss” scenarios after burn 5, the “loss” scenario values on average contained less than half (45.93%) of the “no loss” post-fire residues. This difference is more pronounced in both pyrogenic and black carbon, with “loss” scenarios containing only 36.44% (pyrogenic C) and 34.35% (black C) relative to “no-loss” scenarios. Ohlson and Tryterud [2007] note that charcoal sediment records are short by a factor of 10 given historic fire return intervals of 80 years over an 8000-year period using charcoal production rates presented in Zachrisson et al., [1996]. This work supports their theory that a large proportion of *in-situ* charcoal degradation may be the result of frequent fires.

Production terms are largely a function of fuel loading and consumption, as evidenced by the differences between burns 2 and 3 (Table 2.1). Burn 2 fuel loadings and subsequent post-fire residue production amounts were slightly higher than burns 3, 4, and 5, thereby producing an inconsistent increase in pyrogenic C and black C. The slight decline in pyrogenic C and black C in the “with loss” scenarios between burns 3 -5 is due to the loss rates associated the fuel bed residues from burn 2 being larger than the production terms associated with burns 3, 4, and 5. These differences in fuel loadings and post-fire residue production represent reality, in which fuel loadings between individual fire events will vary

as a function of time since last fire (e.g. fuel accumulation and decay) and land management strategies which may considerably alter natural fuel beds.

#### 4. Conclusions

Repeated burning can play a large role in black carbon losses if the post-fire residues remain on the soil surface and are not transported offsite or incorporated into the soil matrix far enough to be insulated from future fire events. This study estimated that on average 41% of the charred macro-sized residues and pyrogenic carbon, and 39% of the black carbon, was lost in the first repeated burn event after being converted from organic matter. After 4 repeated fires the charred material was reduced by 80%, pyrogenic carbon 94%, and black carbon 99%, suggesting that under high frequency fire regimes repeated burning events rapidly degrade pre-existing black carbon. Both pyrogenic carbon and black carbon concentrations were depleted through repeated burning, however, black C depletions were greater than pyrogenic C. These trends led to significant differences in the black C to pyrogenic C ratio after the third fire event.

Repeated burning also contributes to the production of new black carbon after each burn. Full accounting of black carbon gains and losses through fire is dictated both by loss rates of the existing black carbon as well as the fuel loading and production of new black carbon. Future efforts to model carbon degradation and accumulation should incorporate losses through repeated burns, as simply adding production values greatly over-estimates net black carbon production after 4 repeated burns. Future studies should also seek to incorporate other mechanisms of degradation (e.g. biodegradation and mineralization).

Several limitations exist in this initial attempt to quantify black carbon loss through repeated burns: *i*: actual residue pyrogenic C and black C concentrations for residues < 6mm

in size are assumed to be similar to concentrations of those residues collected through burning of a masticated fuel bed and future studies should explore the use of isotopic tracers for complete accounting of the fuel bed residues, *ii*: loss rates used in the modeled carbon budget are based entirely on loss rates for charred particles >6mm, and future experimental studies should seek to utilize isotopic tracer elements to characterize smaller residues' loss through repeated burning *iii*: carbon budgets are highly dependent on the mass of pre-fire fuels available for consumption, using loss/gain curves produced in this study may not effectively represent production/loss rates associated with other types of fuel types and fire behavior. Despite these limitations, this study highlights the importance of repeated burning as a key pyrogenic C and black C loss mechanism, as well as inherent complexities that arise when constructing a pyrogenic C black C budget which includes repeated burning.

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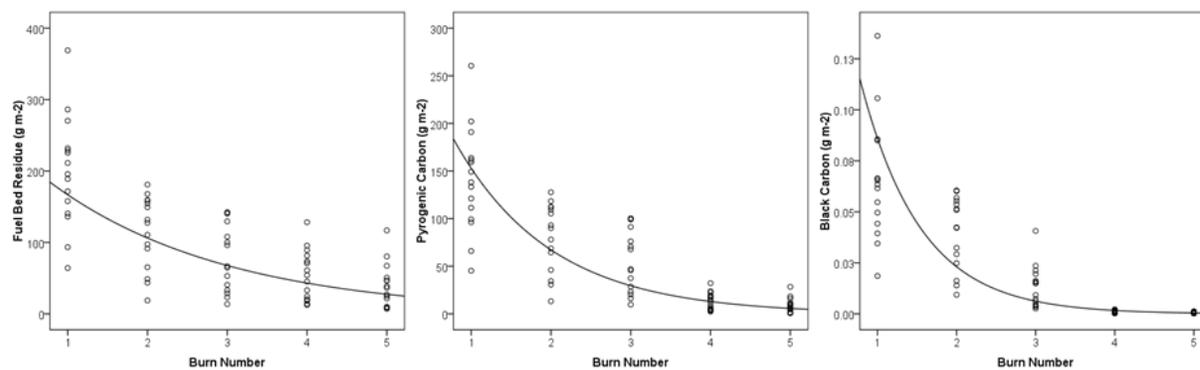
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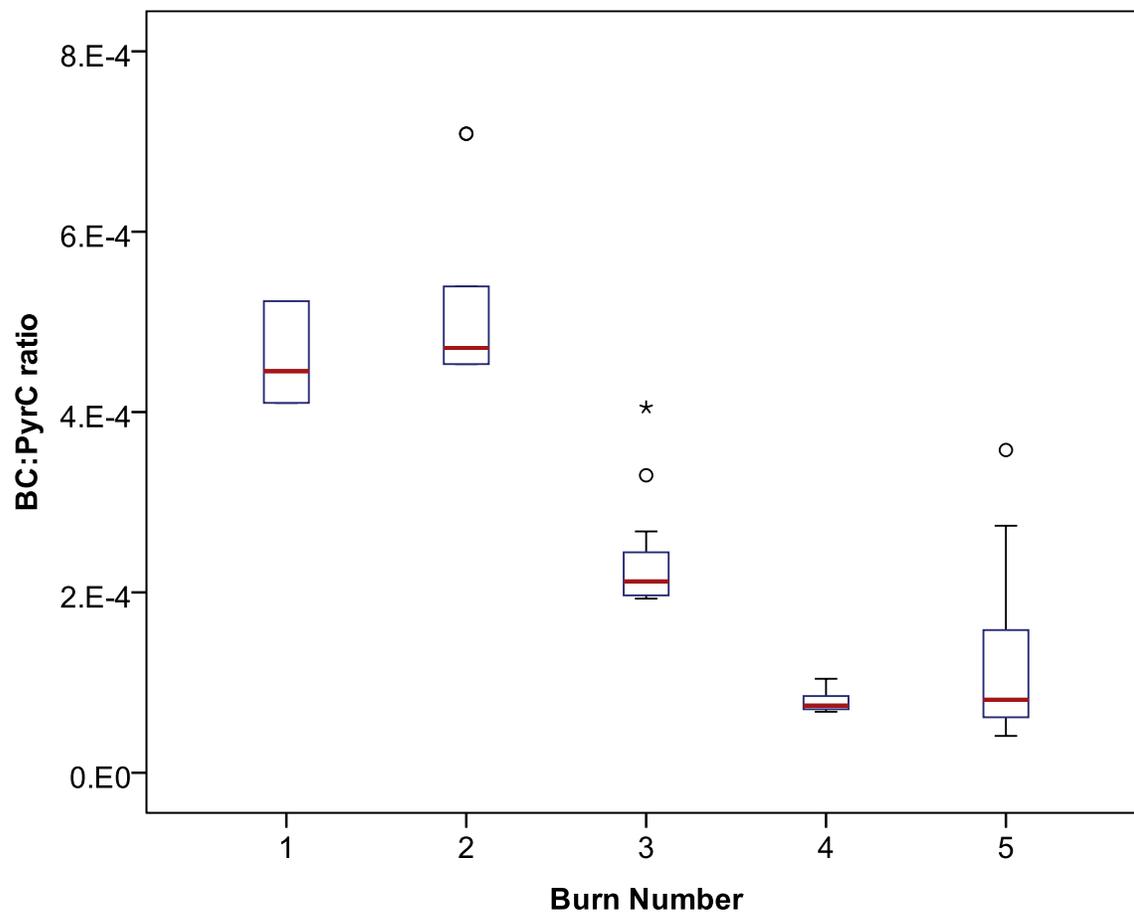
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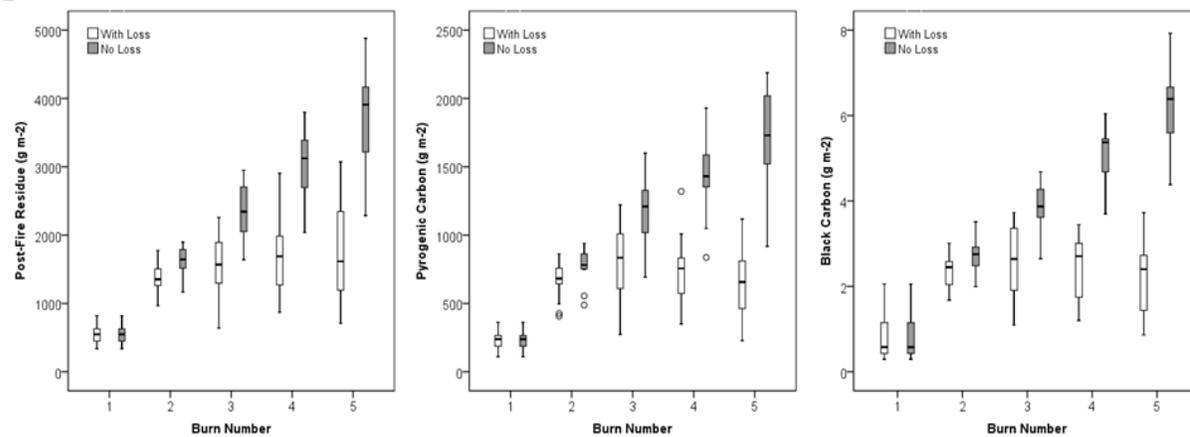
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**Figures:**

**Figure 2.1:** Loss curves for the fire-altered macro charcoal particles, pyrogenic C, and black C. Curves were modeled using exponential regression through the formula:  $y = e^{(-kt)}$ .



**Figure 2.2:** The black carbon to pyrogenic carbon ratio through the 5 repeated burns. The ratio decreases substantially on the 3<sup>rd</sup> burn, as black carbon is preferentially removed from the post-fire residues.



**Figure 2.3:** Two hypothetical carbon budgets shown for post-fire residues, pyrogenic C and black C - one scenario with loss rates included, and the other without loss rates for post-fire residues, pyrogenic carbon, and black carbon (n =15). Loss rates are based on macro-charcoal particle loss through repeated burning.

**Tables:****Table 2.1** Mean (SD) fuel bed characteristics and burn conditions for the burns (n = 15 for each burn number).

Burn Number	Bulk Density (kg m <sup>-3</sup> )	Fuel Loading (kg m <sup>-2</sup> )	Consumption (%)	Fuel Moisture (%)	Temperature (°C)	Relative Humidity (%)
1	102.10 (9.28)	2166.30 (78.65)	90.56 (2.57)	9.98 (3.52)	20.34 (1.00)	38.41 (12.29)
2	58.74 (6.34)	783.02 (90.16)	45.5 (13.07)	9.66 (3.85)	16.69 (2.66)	36.07 (10.98)
3	48.81 (8.37)	658.43 (74.93)	57.41 (18.14)	11.03 (3.28)	21.54 (2.9)	34.26 (5.24)
4	45.87 (4.39)	651.23 (36.32)	57.28 (15.44)	9.49 (4.59)	25.41 (5.18)	30.17 (6.88)
5	52.53 (16.84)	655.24 (47.72)	61.76 (18.05)	10.22 (4.68)	21.48 (2.3)	33.61 (6.41)

**Table 2.2:** Mean (SD) rates for the post-fire residues, pyrogenic C, and black C and associated loss rates (n=15) for the > 6mm charred residues. A repeated measures ANOVA was used ( $\alpha=0.05$ ), and homogenous subsets marked by: a,b,c as identified by Bonferonni post-hoc analysis. Unstandardized slope coefficients (SE) and  $r^2$  for exponential regression analysis are also shown.

Burn Number	Residues (g m <sup>-2</sup> )	Percent Remaining	Pyrogenic Carbon (g m <sup>-2</sup> )	Percent Remaining	Black Carbon (g m <sup>-2</sup> )	Percent remaining
1	198.07 (77.29) a	100.00	139.86 (54.58) a	100.00	6.51E-02 (2.94E-02) a	100.00
2	113.74 (50.93) b	56.59 (17.08)	80.25 (35.93) b	56.54 (17.06)	3.99E-02 (1.77E-02) b	63.40 (22.97)
3	78.78 (46.58) c	37.63 (14.97)	55.56 (32.86) c	37.59 (14.95)	1.36E-02 (1.02E-02) c	20.45 (13.42)
4	54.79 (34.92) d	26.60 (13.31)	13.38 (8.9) d	9.09 (4.87)	1.00E-03 (6.22E-04) d	1.56 (0.82)
5	39.46 (30.68) e	19.46 (13.32)	8.73 (7.62) e	5.94 (4.79)	6.58E-04 (3.61E-04) d	1.06 (0.57)
p-value	<0.001	-	<0.001	-	<0.001	-
$\beta$	-0.451 (0.057)	-	-0.822 (0.066)	-	-1.315 (0.067)	-
R <sup>2</sup>	0.464	-	0.681	-	0.840	-

**Table 2.3:** Pyrogenic C (n=9) and black C (n=3) characteristics through 5 repeated burns and p-values associated with repeated measures ANOVA ( $\alpha = 0.05$ ). Homogenous subsets marked by: a,b,c as identified by the Bonferonni post-hoc test.

Burn Number	Pyrogenic Carbon			Black Carbon		
	$\delta^{13}\text{C}$	%C	C:N	$\delta^{13}\text{C}$	%C	C:N
1	-26.96 (0.64)	70.61 (4.53)	262.04 (87.48)	-23.54 (3.51)	0.97 (1.46)	5.14 (6.21)
2	-26.99 (0.44)	70.55 (2.38)	277.72 (166.89)	-20.78 (1.01)	1.06 (0.14)	8.77 (3.86)
3	-27.08 (0.28)	70.53 (1.24)	239.47 (113.26)	-22.37 (0.77)	0.95 (0.11)	3.95 (2.89)
4	-26.75 (0.64)	68.00 (2.03)	167.89 (33.9)	-22.86 (0.46)	0.05 (0.02)	0.73 (0.53)
5	-26.92 (0.40)	67.53 (2.53)	237.87 (64.06)	-25.86 (3.46)	0.40 (0.58)	4.06 (5.60)
<i>p-value</i>	<i>0.67</i>	<i>0.17</i>	<i>0.23</i>	<i>0.15</i>	<i>0.54</i>	<i>0.32</i>