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- 1 **Title:** Replacing time with space: Using laboratory fires to explore the effects of repeated
- 2 burning on black carbon degradation

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4 Suggested Running Head: Repeated burning on black carbon residence times

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22 Abstract

- Soil organic matter plays a key role in the global carbon cycle, representing three to four times
- 24 the total carbon stored in plant or atmospheric pools. Although fires convert a portion of the
- 25 faster cycling organic matter to slower cycling black carbon (BC), abiotic and biotic degradation
- 26 processes can significantly shorten BC residence times. Repeated fires may also reduce residence
- 27 times, but this mechanism has received less attention. Here we show that BC exposed to repeated
- experimental burns is exponentially reduced through four subsequent fires, by 37.0, 82.5, 98.6,
- and 99.0% respectively. Repeated burning can thus be a significant BC degradation mechanism,
- 30 particularly in ecosystems where burning rates are high, relative to BC soil incorporation rates.
- We further consider loss rates in the context of simulated BC budgets, where 0-100% of BC is

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protected from subsequent fires, implicitly representing ecosystems with varying fire regimes and BC transport and incorporation rates. After five burns, BC storage was as much as 338%

lower than predicted if degradation from burning was ignored. These results illustrate the importance of accounting for BC loss from repeated burning, further highlighting the potential conflict between managing forests for increasing soil carbon storage vs. maintaining historic fire regimes.

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Keywords: carbon storage, ecosystems, fire regimes, soil incorporation, CTO-375

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Table of Contents Summary:

- We highlight via a laboratory experiment the potential of repeated burns to reduce black carbon
- residence times. Our results indicate that for black carbon that remains in-situ to be most
- effective as a net carbon sink, it must be incorporated deep into the organic layer or into the
- 45 mineral soil matrix prior to subsequent burning.

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Introduction

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Globally, soil carbon represents a large and persistent carbon sink, partially offsetting increasing concentrations of atmospheric carbon dioxide (Schimel et al. 1994; Forbes et al. 2006). Biomass burning converts a portion of the faster cycling organic matter to slower cycling black carbon (Lehmann et al. 2008) that has been shown to be resistant to biologic degradation due to changes in its chemical structure (Schmidt and Noack 2000; Masiello 2004). Increased fire activity is predicted for many ecosystems in response to climate change and will likely lead to significant changes in the global carbon cycle (Chapin III et al. 2000; Westerling et al. 2006; Moritz et al. 2012; Flannigan et al. 2013; IPCC 2013). Given the potential for long-term carbon storage, this process has received significant attention in recent decades (Goldberg 1985; Preston and Schmidt 2006), especially given the growing interest in black carbon's contribution to the soil organic carbon (SOC) pool which can exceed 50% in some ecosystems (Lehmann et al. 2008; Schmidt et al. 2011; Santín et al. 2015a). Radiocarbon dating of black carbon in soils have shown residence times on the order of 100's~1000's of years (Schmidt et al. 2002, 2011; Preston et al. 2006; Kuzyakov et al. 2009; Zimmerman 2010). However, abiotic and biotic degradation processes can significantly shorten black carbon residence times (Czimczik and Masiello, 2007; Zimmerman, 2010). Repeated biomass burning has been postulated to also reduce residence times of black carbon (Ohlson and

biomass burning has been postulated to also reduce residence times of black carbon (Ohlson and Tryterud, 2000; Rovira *et al.* 2009), but this mechanism has received less attention (Santín *et al.*

2013). However, in forested ecosystems that have a high propensity to produce black carbon

through combustion of woody fuels (Hurteau and Brooks, 2011), the typical time between fires is

of the order of decades to centuries. This temporal scale limits the ability to observe and quantify

this process in a field setting, thus emphasizing the need for an experimental approach.

Black Carbon Cycling

Fire altered carbon from biomass burning exists on a recalcitrance gradient, from partially charred vegetation to soot (Masiello 2004; Smith and Hudak 2005; Preston and Schmidt 2006; Keiluweit *et al.* 2010). Given research into black carbon covers soil science, biogeochemistry, and fire science; differing terminology occurs and can lead to some confusion. As described in Preston and Schmidt (2006), the term pyrogenically altered carbon is used to

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describe the entire spectrum of carbon that has been thermally altered by the fire, whereas black carbon (BC) often only refers only to a narrow range of pyrogenic carbon produced through thermal exposure. Specifically, BC is defined here as the highly recalcitrant material that exhibits significantly lowered H:C and O:C ratios (Kuhlbusch *et al.* 1996; Hatten and Zabowski, 2009; Brewer *et al.* 2013). Pyrogenic organic matter (PyOM) is another widely used term that has been used to describe black carbon (Santin *et al.* 2015a). A source of confusion may arise from the term pyrogenic carbon, which is used to describe black carbon (Santin *et al.* 2013) due to its closeness to the Preston and Schmidt (2006) terminology. In this study, we do not advocate the usage of a specific set of terminology but rather elect the follow the terminology associated with the analytical BC calculation method used in this paper (Hatten and Zabowski, 2009).

The coupling of BC production, soil incorporation rates, and BC loss via combustion creates a complex relationship between the frequency of burning in an ecosystem and total BC storage. The molecular composition alone cannot singularly predict carbon's persistence in soils; rather, ecosystem processes and soil matrix interactions play important roles in its longevity (Czimczik and Masiello 2007; Jenkins et al. 2014). Specifically, the physical protection of BC. for example via soil incorporation or off-site transport, is required for it to be preserved over geologic time scales (DeLuca and Aplet 2008; Fang et al. 2014). With each new fire BC is generated, but the existing BC from prior fires may also be consumed if it remains near the soil surface and exposed to the fire (Ohlson and Tyrterus 2000; Czimczik et al. 2003; Rovira et al. 2011). Two recent field two studies measured consumption of pre-existing BC (charcoal) by fire in contrasting environments. Santin et al. 2013 found median mass losses <15% of BC samples placed within the surface of the organic layer consumed in a boreal forest fire and Saiz et al. (2014) reported average mass losses <8% of BC and on the soil surface in a prescribed fire in open sayannah woodland. Schmidt and Noack 2000) suggest that thermal degradation not usually achieved at mineral soil depths > 30 mm. However, research quantifying soil incorporation rates of pyrogenic carbon are limited (Nocentini et al. 2010). Preliminary projections suggest that it takes decades to centuries for fire residues to be adequately incorporated into a soil matrix to ensure protection from fires (Eckmeier et al. 2007; Lehmann et al. 2008), considerably longer than fire return intervals in most dry temperate forests (Littel et al. 2009). Given fire frequencies in many ecosystems are expected to change due to climate

(Flannigan *et al.* 2013), it is important to address how repeated burning may influence BC pools (Czimczik and Masiello 2007; Schmidt *et al.* 2011; Santin *et al.* 2015b). For the first time, we present results from a controlled laboratory experiment to quantify how exposure to repeated fire events degrades BC pools. We hypothesize that neglecting the BC losses associated with repeated burning may lead to significant overestimates of soil BC storage. In turn, accounting for BC losses as a function of repeated burning will lead to significantly less BC available for incorporation into the passive SOC pool, and these losses will likely have significant impacts on net soil BC estimates.

Methods

Sample collection and construction of fuel beds

To test our hypothesis we selected woody surface fuels that had been controlled for their particle size and moisture content, allowing for a controlled laboratory combustion experiment. The constructed fuel beds represented a so-called masticated fuel matrix within a western North American temperate conifer forest, dominated by western white pine (*Pinus monticola*), Douglas-fir (*Pseudotsuga menziesii*), and lodgepole pine (*Pinus contorta*). Full details on sample collection and fuel bed construction are outlined in a prior study (Brewer *et al.* 2013). Fuels were collected from an 8 ha stand within the Clearwater National Forest (latitude: 46.80N, longitude: 119.47 W) that included white pine (*Pinus monticola*), Douglas Fir (*Pseudotsuga menzisii*), and lodgepole pine (*Pinus contorta*). During mastication the woody particles were chipped into predominately small-diameter particles (<7.6 cm). Fuels were collected following the sampling protocols in Hood and Wu (2006). Fifteen fuel beds were constructed representing a typical woody surface fuel loading (5835 g m⁻²) observed in mesic mixed conifer systems of the northwestern United States (Kreye *et al.* 2014; Sparks *et al.* in review).

Initial burn methodology

Fire experiments were conducted at the Idaho Fire Initiative for Research and Education (IFIRE) laboratory located in a climatically controlled environment, shielded from weather effects (Brewer *et al.* 2013; Smith *et al.* 2013). The experimental burn and residue collection and analysis methodologies followed the procedures detailed by Brewer *et al.* (2013). Burns were

considered to be complete when mass loss had ceased, as measured with a Sartorius EB Series scale (precision: 1 g, range: 0.0005-65.0000 kg, Goettingen, Germany). Following combustion, post-fire residues were sieved into > 6 mm, 1-6 mm, and < 1 mm size classes and weighed using a Sartorius scale (precision: 0.1 g, range: 0.1-2,000.0 g), with two ~ 1 g sub-samples collected for BC proportion analysis. BC was quantified using thermo-chemical methods adapted from CTO375 protocols, which isolates the biologically resistant portion of the pyrogenic carbon (Hatten and Zabowski 2009; Sánchez-García *et al.* 2012). Following elemental analysis of BC proportions (CTO375_{BC(%)}), the BC mass (BC_{mass}, g) was calculated by (Equation 1; Hatten and Zabowski 2009):

$$BC_{mass} = CTO375_{BC(\%)} * [pre_{mass} - post_{mass}]$$
 [1]

Where, pre_{mass} (g) and $post_{mass}$ (g) are the original fuel loading and mass of post-fire residues respectively.

Repeated burns methodology

To quantify how the post_{mass} residues from the initial burns persisted under subsequent burns, each burnt fuel bed (n=15) was subsequently exposed to four consecutive burn trials. We acknowledge that ideally we should observe BC incorporation and losses in a field setting (e.g., Santin *et al.* 2013), however we contend that this experimental approach allows us to simulate long fire return intervals that otherwise could only be inferred form modeling studies. In each of the subsequent burn trials a consistent litter fall was included as a layer of solely pine needles consisting proportionally (by mass) of lodgepole pine and ponderosa pine (*Pinus ponderosa*), which are common early seral species in the study region. The pine needles were added to the top of the fuel bed and selected in lieu of other litter components due to ease of replication, with the mass of needles increased to account to other missing components (e.g. leaves, twigs). These pine needle fuel beds were constructed to resemble an upper limit of litter fuel loading (1,700 g m⁻²) in temperate conifer forests throughout western U.S. and Canada (Law *et al.* 2003, Hyde *et al.* 2011). Fuel moisture was controlled by placing prepared fuel beds in a drying oven prior to combustion (Table 1a; Brewer *et al.* 2013).

In each repeated burn after the initial characterization, only the residues > 6 mm in size underwent additional elemental analysis for assessing BC proportions and were carried forward into the subsequent burn trials where these particles were mixed throughout the pine needle fuel beds. Residues < 6 mm were not carried forward, as these were indistinguishable from the newly burnt pine needles. To calculate percent BC remaining [Equation 2] in subsequent burns, BC masses were standardized against BC produced in the initial burn, by:

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$$BC_{Ri} = \frac{BC_1 - BC_i}{BC_1}$$
 [2]

Where, BC_{Ri} is the normalized remaining BC after burn number i, BC_1 is the BC produced from burn number 1, BC_i is the remaining BC after burn number i, and i represents the burn number from 2 to 5. Since grass fires likely produce charcoal residues smaller than 6 mm, the conclusions of this experiment are limited to ecosystems with woody vegetation (i.e. trees and shrubs), which represents a continuum from savannah to mesic forest.

Statistical analysis and modeling

A repeated measures ANOVA was used to test for differences in post-fire residue and BC masses for each burn trial. When Mauchly's sphericity assumption was not met, the Greenhouse-Geisser statistic was used. A Bonferroni post-hoc test was used to compare the main effect of burn number. To generalize our results and construct a range of partially protected BC budgets, we fit a negative exponential model, robust to outliers, to the individual mass-loss percentages of the exposed > 6 mm residues: $y = a^{bx}$, where y is the predicted remaining BC mass (% of the original mass), and x is the burn number (where x = 1 for the initial burn). When a = 259.0 (239.5 - 278.6, 95% prediction bounds) and b = -0.9476 (-1.008 - -0.8877) this model explained 98% of the variability in our observed data. The observed BC mass loss rate was used to develop a BC budget through the five burns. Further, a series of hypothetical BC budgets, representing varying degrees (0-100%) of protection of the total BC produced in the initial burn are produced

and discussed. Statistical analyses were conducted using IBM SPSS predictive analytics software (version 19), and Matlab technical computing software (version 7.11.1). For this modeling the BC produced in the combustion of the added litter layer is not included, as it is indistinguishable from the fine woody BC.

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Results and Discussion

Following the initial burns, ~61, 31, and 8% of the BC produced were in the < 1 mm, 1-6 mm, and > 6 mm residue size classes respectively. The > 6 mm BC from the initial burns declined significantly across the four subsequent burns (Table 1b, Figure 1). Following Burn 5, only 1% of the exposed BC produced in the initial burn (Burn 1) remained. Integrating the charred residues throughout the litter layer probably made the charred particles more susceptible to thermal degradation. However, in a field setting charred residues could remain at the interface of the O-horizon and mineral soil or the material could be mixed throughout the O-horizon depending on the pedoturbation intensity, eventually the char will become incorporated into mineral soil (Gavin 2003). Consequently, our estimates are likely to represent an upper bound of losses associated with repeated burning, however more research is needed on pedoturbation within the O-horizon. Moving the charred particles to the bottom of the litter horizon or placing them below the soil surface to simulate soil incorporation could have resulted in lower loss rates (Santín et al. 2013). Regardless, our results support the prevailing hypothesis that in forest types with high-frequency burning and little to no soil incorporation, repeated burning can be a significant mechanism for BC loss (Ohlson and Tryterud 2000; Preston and Schmidt 2006; Rovira et al. 2009). Our results also indicate that in as few as two repeated burns, the majority (~80%, Table 1b, Figure 1) of the exposed BC produced in an initial fire can be lost. Given that the best estimates of BC loss rates through biotic and abiotic (non-pyric) mechanisms range from < 1% to 37% over 100 years (Zimmerman 2010), our results highlight repeated burning as a potentially significant mechanism of carbon loss.

To estimate the compounding effects of BC loss through repeated burning, we used the experimental loss rates of the exposed carbon (Figure 1) to construct a BC budget spanning five burns (Figure 2; Ohlson and Tryterud 2000; Czimczik and Masiello 2007; Zimmerman 2010). This budget assumes all material < 1 mm is protected from future burning, implicitly

representing immediate off-site wind transport like is common in grassland and savannah ecosystems or incorporation of fine particles into the soil and litter matrix (Rumpel *et al.* 2009). Protecting the < 1 mm BC left 39% of the BC produced in an initial burn available for further thermal degradation. This scenario also assumes that an equivalent masticated fuel loading was reached between each burn, representing a best case estimate for dry forest types, were net BC increases at a near-linear rate of approximately 70% per burn (Figure 2). By the fifth burn, BC storage is 381% of that created in the initial burn, whereas an estimate ignoring BC loss from repeated burning would predict a value of 500%. The "missing" 119% represents the tradeoff between generating new BC while consuming existing BC with each successive burn. We acknowledge that a full accounting of the residual size categories would provide more accurate estimates of BC loss rates, however given analytical limitations of separating these fine char fractions from pine needle residues in the repeated burns, this was not feasible.

The degree to which repeated burning impacts a BC budget inherently reflects assumptions on BC protection from future burning (e.g., via soil incorporation or off-site transport; Rumpel *et al.* 2009; Dittmar *et al.* 2012; Santín *et al.* 2013). To generalize our results and explore this sensitivity, we used the fitted model in Figure 1 to calculate net BC storage under five different scenarios, where 0%, 25%, 50%, 75%, and 100% of the BC produced in the initial burns is protected from future burning (Figure 3). As expected, BC budgets are highly sensitive to protection rates: at 0% protection, net BC asymptotes around 160% after four burns, implying an upper limit to BC storage. Under the scenario with 75% BC protected, values fail to asymptote and reach 416% following the fifth burn (Figure 3).

Implicitly, these scenarios represent a series of generalized environmental conditions that dictate both BC protection rate (% yr⁻¹) and the rate of burning (fire yr⁻¹) in a given ecosystem. For example, while savanna ecosystems are frequented by fires every 3-5 years, mesic forests can exhibit fire return intervals of 200+ years. Although less well known, soil incorporation and off-site wind transfer rates of BC in these systems likewise vary (Rumpel *et al.* 2009; Nocentini *et al.* 2010; Kasin and Ohlson 2013), principally due to differences in soil exposure, topography, precipitation, temperature, and wind regimes. If burning rates are faster than the protection rate required to safeguard BC, then most BC produced in a burn will still be exposed during subsequent burns. This may represent a scenario of 0% or 25% BC protection, which may be

comparable to the short fire return interval found in savannah systems if off-site transport through wind and water erosion is minimal; a scenario that may not be commonplace given these particles are often considered very susceptible to offsite transport by wind and water processes in grasslands and savannahs. In contrast, the longer fire return intervals of boreal forests may allow time for BC to be incorporated far enough into the litter and duff or mineral soil to be protected during subsequent burns; this ecosystem is more likely represented by a scenario of 75% or 100% BC protection (Santín *et al.* 2015).

The ratio of these two processes (fires %-1), i.e., the rate of burning (fire yr-1) and rate of BC protection (% yr-1), will determine the sensitivity of soil BC budgets to repeated burning. Assessment of this ratio will enable studies to determine if and when net BC storage reaches an asymptote, but will require understanding the protection and production rates of residues of different sizes in different ecosystems. If frequent fire consumes black carbon faster than it can be protected by soils or off-site transport, then those forested systems with short fire return intervals would have lower amounts of black carbon compared to forested systems with long fire return intervals. While unexplored in their study, this hypothesis is generally supported by Jauss *et al.* (2015) whose data show that the black carbon content of the forested soils has a significant relationship with fire return interval (r²=0.452). However, the per-fire production rate of black carbon is a function of other factors such as fire severity, fire return interval, and net primary productivity which could account for some of the unexplained variability in this relationship.

Ultimately, these processes likewise dictate the feasibility of using fuel treatments and fire hazard management (prescribed, wildland fire use fires, etc.) as tools to increase soil BC storage (Deluca and Aplet 2008; Santín *et al.* 2015b). Given the tradeoff between BC production and consumption in subsequent burns, maintaining "natural" fire regimes in ecosystems historically characterized by high-frequency fires (e.g., burning once every several years to decades), may be at odds with maximizing soil BC storage.

Conclusion

This study highlights the potential importance of physical degradation of BC through repeated burning, adding combustion as a key mechanism to previous work demonstrating BC loss through biological and physical degradation (Preston and Schmidt 2006; Schmidt *et al.*

- 287 2011). For BC that remains in-situ to be most effective as a net carbon sink, it must be
- incorporated deep into the organic layer or into the mineral soil matrix prior to subsequent
- burning. Our work is a first step towards quantifying BC loss rates from repeated burning to
- more accurately model long-term BC storage in soil organic pools, but projecting the long-term
- impacts on carbon budgets requires more precise estimates of BC protection rates (Santin et al.
- 2015b). Biogeochemical models that track BC should be sensitive to the combined effects of
- burning, soil incorporation, and off-site transport rates, as exemplified by the ratio of these
- 294 processes.

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Table 1. (A) Mean (SD) fuel bed characteristics and burn conditions for the five experimental burns (n = 15 replicates for each burn number). (B) Median (SD) production and loss rates associated with the post-fire residues and BC (n=15). Burn 1 represents the initial fire, which produced all of the > 6 mm residues used in the subsequent burns represented as burns 2-5. All p-values <0.001 reported from repeated measures ANOVA. Homogenous subsets as identified by Bonferonni post-hoc analysis are identified as a, b, c, d, and e.

A)	Burn Number	Bulk Density (kg m ⁻³)	Fuel Loading (g m ⁻²)	Consumption (%)	Fuel Moisture (%)	Temperature (°C)	Relative Humidity (%)
	1	102.1 (9.3)	5829.7 (211.7)	90.6 (2.6)	10.0 (3.5)	17.8 (7.3)	38.4 (12.3)
	2	58.7 (6.3)	2107.2 (242.6)	45.5 (13.1)	9.7 (3.9)	16.7 (2.7)	36.1 (11.0)
	3	48.8 (8.4)	1771.9 (201.7)	57.4 (18.1)	11.0 (3.3)	21.5 (2.9)	34.3 (5.2)
	4	45.9 (4.4)	1752.5 (97.7)	57.3 (15.4)	9.5 (4.6)	25.4 (5.2)	30.2 (6.9)
	5	52.5 (16.9)	1763.3 (128.4)	61.8 (18.1)	10.2 (4.7)	21.5 (2.3)	33.6 (6.4)

B)	Burn Number	Residues (g m ⁻²)	Residue Remaining (%)	BC (g m ⁻²)	BC Remaining (%)
•	1	198.1 (77.3) a	100.0 (0.0)	0.0650 (0.0290) a	100.0 (0.0)
	2	113.7 (50.9) b	55.6 (17.1)	0.0400 (0.0180) b	63.0 (23.0)
	3	78.8 (46.6) c	38.5 (15.0)	0.0140 (0.0100) c	17.5 (13.4)
	4	54.8 (34.9) d	24.2 (13.3)	0.0010 (0.0006) d	1.4 (0.8)
	5	39.5 (30.7) e	15.7 (13.3)	0.0007 (0.0004) d	1.0 (0.6)

Figure 1. BC loss with repeated burning. Burn number 1 represents total carbon produced after the initial burn (100%). For each repeated burn (Burn number 2-5), 15 replicates are shown as observations. The solid black line represents a robust fit of the model $y = a e^{bx}$, and the dashed lines represent 95% prediction intervals. The fitted model explains 98% of the variability in the observations ($r^2_{adj} = 0.98$), when a = 259.0 and b = -0.9476.

 Figure 2. BC budget based on experimental observations. The net BC contributed to the budget of each burn number is tracked via varying shades of grey. Each burn contributes 100% of the BC generated in the initial burn, and 61% (39%) of this BC is protected from (exposed to) degradation in subsequent burns.

Figure 3. BC budgets based on varying modeled scenarios. Using the fitted model in Figure 1 to calculate loss rates, each budget assumes that a varying level of BC is protected from subsequent burning (from 0-100%). Each scenario implicitly represents varying soil incorporation rates and fire frequencies across a range of fire-prone ecosystems.