



# Distribution of black carbon in ponderosa pine forest floor and soils following the High Park wildfire

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Received: 12 September 2014 – Published in Biogeosciences Discuss.: 5 December 2014

Revised: 8 April 2015 – Accepted: 14 April 2015 – Published: 22 May 2015

**Abstract.** Biomass burning produces black carbon (BC), effectively transferring a fraction of the biomass C from an actively cycling pool to a passive C pool, which may be stored in the soil. Yet the timescales and mechanisms for incorporation of BC into the soil profile are not well understood. The High Park fire (HPF), which occurred in northwestern Colorado in the summer of 2012, provided an opportunity to study the effects of both fire severity and geomorphology on properties of carbon (C), nitrogen (N) and BC in the Cache La Poudre River drainage. We sampled montane ponderosa pine forest floor (litter plus O-horizon) and soils at 0–5 and 5–15 cm depth 4 months post-fire in order to examine the effects of slope and burn severity on %C, C stocks, %N and BC. We used the benzene polycarboxylic acid (BPCA) method for quantifying BC. With regard to slope, we found that steeper slopes had higher C:N than shallow slopes but that there was no difference in BPCA-C content or stocks. BC content was greatest in the forest floor at burned sites (19 g BPCA-C kg<sup>-1</sup> C), while BC stocks were greatest in the 5–15 cm subsurface soils (23 g BPCA-C m<sup>-2</sup>). At the time of sampling, unburned and burned soils had equivalent BC content, indicating none of the BC deposited on the land surface post-fire had been incorporated into either the 0–5 or 5–15 cm soil layers. The ratio of B6CA:total BPCAs, an index of the degree of aromatic C condensation, suggested that BC in the 5–15 cm soil layer may have been formed at higher temperatures or experienced selective degradation relative to the forest floor and 0–5 cm soils. Total BC soil stocks were relatively low compared to other fire-prone grassland and boreal forest systems, indicating most of the BC produced in this system is likely lost, either through erosion events, degradation or translocation to deeper soils. Future work ex-

amining mechanisms for BC losses from forest soils will be required for understanding the role BC plays in the global carbon cycle.

## 1 Introduction

While pyrogenic or black carbon (BC) is now recognized as a ubiquitous soil carbon (C) fraction, it is one of the least understood components of the terrestrial C cycle. Every year, fire burns approximately 10–15 × 10<sup>6</sup> ha of boreal and temperate forest and more than 500 × 10<sup>6</sup> ha of tropical and subtropical forests and savannas (Goldammer and Crutzen, 1993; Knicker, 2011), during which 0.12 to 9.5 % of the burned biomass is converted to BC (Forbes et al., 2006). Black C is utilized by soil microbes, but at a slow rate (Santos et al., 2012); it generally resides in the soil for a long time (from centuries to millennia; Singh et al., 2012), acting as a long-term C sink, with a potential negative feedback on climate warming. However, BC stocks in soils are not only related to BC production rate and decomposition but may also be lost through runoff, leaching or burning (Czimczik and Masiello, 2007; Foereid et al., 2011); thus, BC stocks are strongly dependent on surface topography and soil physical-chemical environment (Bird et al., 2015; Knicker, 2011).

BC persistence and dynamics in soil seem to be controlled by mechanisms similar to those that control soil organic matter dynamics including inherent chemical recalcitrance and organo-mineral interactions (Knicker, 2011). Persistent BC particles in soils are composed of a refractory, aromatic core and a reactive, oxidized patina (Keiluweit et al., 2010; Lehmann et al., 2005) characterized by carbonyl and

carboxyl functionalities (Cheng et al., 2006, 2008). The degree of condensation of the aromatic core has been shown to be quite variable (McBeath and Smernik, 2009; Wiedemeier et al., 2015b) but can be broadly characterized as dominated by C in condensed aromatic rings resistant to decomposition (Baldock and Smernik, 2002). Besides its inherent chemical recalcitrance, BC stabilization in soils likely occurs through bonding to minerals, which is thought to be the most persistent mechanism of SOM (soil organic matter) stabilization (von Lutzow et al., 2006). The presence of carboxyl functionalities on BC surfaces provides “teeth” available to chelate soil aluminum and iron, creating BC mineral complexes that are highly refractory to microbial decay and have longer mean residence times than non-mineral-associated BC (Christensen, 1996; von Lutzow et al., 2006).

In order to become stabilized in soils, BC must first be transferred from burned surface material to the subsurface, and the process of incorporation will be strongly related to surface topography. The shape of a landscape and propensity for erosion versus deposition is dependent upon several variables including bedrock composition, slope, elevational gradients in temperature and precipitation, and disturbance history such as the frequency of wildfires. While the strong relationships between geomorphology, soil erosion and sediment transport are fairly well understood (Ritchie and McCarty, 2003; Slater and Carleton, 1938), the relationship between soil erosion and the fate of different components of SOM that are eroded, including BC, is relatively unknown (Bird et al., 2015; Rumpel et al., 2006).

The difficulty in measuring BC contributes to our limited understanding of its transport processes and function in the global C cycle. Because BC exists along a continuum of combustion products, from charred biomass to soot, with differing physical and chemical features, no single method can accurately quantify total BC content (Hammes et al., 2007; Masiello, 2004). Visual counts of charcoal, resistance to oxidation methods, nuclear magnetic resonance (NMR) spectroscopy or the quantification of BC-specific molecular markers (e.g., benzene polycarboxylic acids, BPCAs) have each been employed for the quantification of BC. While each approach has advantages and disadvantages, the BPCA method has been shown to yield conservative estimates of BC with charred inputs and more consistent results than many other quantification methods (Hammes et al., 2007). Moreover, the BPCA method yields additional information about BC quality related to its degree of aromatic condensation and aromaticity (Schneider et al., 2010, 2013; Wiedemeier et al., 2015a; Ziolkowski et al., 2011).

A few estimates exist of BC production after fire (Santín et al., 2012), as well as of BC stocks in soils for different ecosystems (Bird et al., 1999; Cusack et al., 2012; Schmidt et al., 2002). Yet, estimates of BC production and losses are not balanced (Czimczik and Masiello, 2007; Rivas et al., 2012), clearly identifying our lack of understanding and the need

for a full accurate accounting of BC dynamics after fire at the watershed level.

Between 9 and 24 June 2012, the High Park fire (HPF) burned more than 35 000 ha in northern Colorado along the Cache la Poudre (CLP) River in an area dominated by ponderosa pine (*Pinus ponderosa*; Fig. 1). The aims of this work were to (1) determine the C and BC stocks, and the proportion of C that was BC, in ponderosa pine forest floor and soils following the HPF; (2) examine the effects of burn severity and landscape slope on soil C, N and proportion of BC; and (3) use the distribution of individual BPCAs to understand the degree of condensation of BC through the soil profile. We expected that BC stocks would be the greatest at high burn severity sites, followed by moderate and then unburned sites, and that the hillslope would have the opposite effect, with lowest BC stocks on the steepest slopes and greatest BC stocks on shallow slopes. We anticipated that BC and C stocks would be greater in the forest floor than in soils and that soil C stocks would be diminished in high burn severity surface soils due to combustion during fire. We also expected that the molecular characteristics of BC would change with depth related to their degree of condensation.

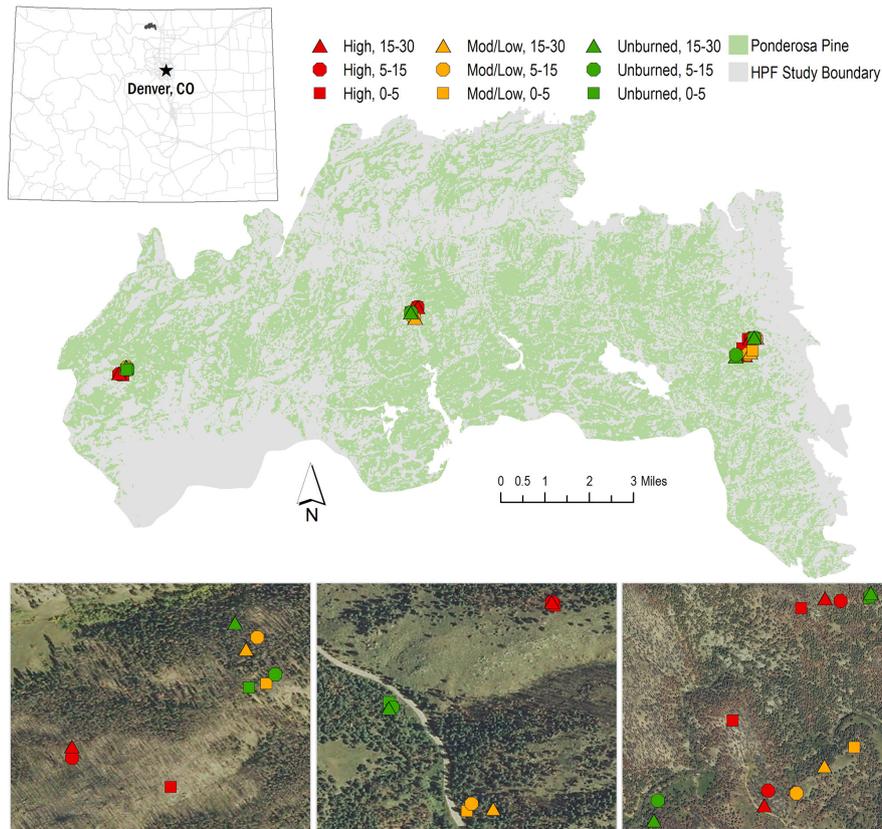
## 2 Materials and methods

### 2.1 Experimental design and site identification

The sites were located within the montane forest (elevation 1750 to 2850 m) of the CLP drainage, which is dominated by ponderosa pine (*Pinus ponderosa*) and Douglas fir (*Pseudotsuga menziesii*) and also includes aspen (*Populus tremuloides*), Rocky Mountain juniper (*Juniperus scopulorum*), lodgepole pine (*Pinus contorta*) and other species (Veblen and Donnegan, 2005). Soils in the montane forests are Alfisols from the great group Cryoboralfs and Mollisols from the suborder Ustolls (Peet, 1981).

The montane ponderosa pine forest has a variable severity fire regime meaning there is a mixture of both high-severity, full- or partial-stand-replacing fires and low-severity, non-lethal, surface fires. The mean return interval is approximately 40 to 100 years, and most fire events have both high- and low-severity components and are caused by a combination of human and lightning strike ignition (Veblen and Donnegan, 2005). A lightning strike started the HPF on 9 June 2012. It burned over 35 000 ha in the mountainous region of the CLP River drainage through early July 2012.

Our study was a fully factorial, randomized block design with four replicate blocks for all treatments plots, including three levels of burn severity (unburned, moderate burn, high burn) and three slopes (0–5, 5–15 and 15–30°), for a total of 36 plots. We opted to constrain the study by slope rather than landscape position (e.g., hilltop versus valley location of flat surface) in order to constrain study site criteria to public lands within the patchy distribution of fire-impacted sites of



**Figure 1.** Location and classification (burn severity and slope) of study sites ( $n = 36$ ) in the dominant ponderosa pine vegetation highlighted in green within the High Park fire burn area.

ponderosa pine vegetation on difficult to access terrain. Geographic information system (GIS) layers of land ownership, slope, fire intensity and burn severity were obtained prior to site location. Potential sampling areas were chosen in state or federal land in areas of homogenous vegetation stands where all slope classes and fire classes were present within a close distance (Fig. 1). Ground truthing was subsequently done to locate each specific slope and burn severity sampling treatment plot. Slopes were determined using a clinometer. Areas were classified as high burn when the fire had burned the entire tree and no needles or small branches remained, the litter layer was consumed in the fire, and there were some small pieces of charcoal throughout the surface layer. Moderate burn areas had ground fire and some crown scorch, but crowns did not burn, at least some needles remained on the trees, and the litter layer remained on the forest floor with some small pieces of charcoal. Unburned areas had no evidence of ground fire and no evidence of burned material on the ground surface.

## 2.2 Forest floor and soil collection

Soil and forest floor samples were collected between October and November of 2012. At each of the 36 experimental

plots, forest floor and soils were collected from within a 20 by 20 cm wooden frame and frame GPS coordinates were recorded. The forest floor layer was sampled first including any litter plus organic soils down to the mineral layer, and then the soil was excavated with a hand shovel separately for the 0–5 and 5–15 cm depth. Due to the high surface variability, four additional forest floor samples and three surface (0–5 cm) soil samples were collected at each site, positioning the frame orthogonally at a distance of 2.5 m from the original position. All forest floor and surface soil samples were pooled by plot.

Due to the extreme rockiness at all of the sampling locations, soil bulk density was determined using pit excavation separately for each depth layer (Page-Dumroese et al., 1999). The volume of the pit was determined using volume displacement with millet seed (detailed description in the Supplement). Soil and forest floor samples were transported to the lab and stored at 4 °C until processing.

## 2.3 Forest floor, soil pretreatment and elemental analyses

In the laboratory, forest floor samples were weighed field-moist and a subsample of each was dried at 105 °C for 48 h

for dry weight correction. Forest floor samples were then air-dried and another subsample taken and heated in a muffle furnace at 600 °C for 12 h to correct forest floor dry weight for ash content. All remaining air-dried forest floor samples were passed through an 8 mm sieve, and any large pieces of plant material were broken up with clippers prior to the samples being ground with a 0.75 mm mesh-screen-equipped Wiley mill and dried overnight at 60 °C.

Soil samples were weighed field-moist and a subsample of each was dried at 105 °C for 48 h for dry-weight correction. Bulk density of each soil depth was calculated as the weight of oven-dry soil with rock removed (Throop et al., 2012) divided by the volume for the depth determined by millet with rock volume removed. Soils were sieved air-dry to 2 mm, and a subsample was oven-dried (105 °C) and finely ground. All the ground, dry, forest floor and soil samples were analyzed for total C and N by an elemental analyzer (LECO CHN-1000; LECO Corporation, St. Joseph, MI, USA) and for BC by the BPCA method as described below.

## 2.4 BPCA analyses

The BPCA method converts condensed aromatic structures to single aromatic rings with variable numbers of carboxylic acid moieties, and a greater degree of condensation (i.e., number of fused rings) correlates with a greater number of carboxylic acid moieties on the individual BPCAs such that more condensed structures result in greater relative abundance of B6CAs and the least condensed BC would result in a greater proportion of B3CAs (Glaser et al., 1998; Wiedemeier et al., 2015a; Ziolkowski et al., 2011). Black C was determined on all forest floor and soil samples using high-performance liquid chromatography (HPLC) equipped with a photo diode array detector to quantify benzene polycarboxylic acids (BPCAs) as described by Wiedemeier et al., 2013. The BPCA method was validated with biochar-amended soils from the field site (see the Supplement). Briefly, 50–150 mg of finely ground, oven-dried sample was digested with 70 % nitric acid for 8 h at 170 °C. The solution was filtered with ashless cellulose filters, an internal check standard of phthalic acid was added to the solution and the filtrate was cleaned by cation exchange resin and freeze-dried. The freeze-dried sample was redissolved in HPLC-grade water. The redissolved solution containing the BPCAs was separated with a reversed stationary phase column (Waters X-Bridge C18, 3.5 µm particle size, 2.1 × 150 mm) using standard gradient conditions. Individual BPCAs were quantified with using a five-point calibration from standard solutions of benzenetricarboxylic acids (1,2,3-B3CA, i.e., hemimellitic acid; 1,2,4-B3CA, i.e., trimellitic acid; 1,3,5-B3CA, i.e., trimesic acid), benzenetetracarboxylic acid (1,2,4,5-B4CA, i.e., pyromellitic acid), benzenepentacarboxylic acid (B5CA) and benzenhexacarboxylic acid (B6CA, i.e., mellitic acid). The B4CA standards that are not commercially available (1,2,3,4-B4CA, i.e., pre-

henitic acid, and 1,2,3,5-B4CA, i.e., mellophanic acid) were identified by their ultraviolet adsorption spectra and quantified using the calibration for 1,2,4,5-B4CA (Yarnes et al., 2011). Previous attempts to calculate a BPCA-C to BC conversion factor have resulted in values that range from 2.27 to 5 and have been difficult to reproduce (Brodowski et al., 2005; Glaser et al., 1998; Ziolkowski et al., 2011). Thus, to simplify empirical comparisons we report values as BPCA-C, either as a proportion of total C or as a stock.

## 2.5 Data analyses

The effects of layer (forest floor, 0–5 and 5–15 cm soil;  $n = 4$  per layer), slope (0–5°, 5–15°, 15–30°,  $n = 4$  per slope) burn severity (unburned, moderate burn, high burn,  $n = 4$  per severity) and all interaction terms on each response variable (soil C, soil N, BPCA C stock, BPCA C as a proportion of total C, and relative abundances of B4CA, B5CA, B6CA and B5CA : B6CA ratio) were compared using the SAS mixed procedure (proc mixed); fixed variables were layer, slope and severity, and block and core were designated as random effects. Post hoc analysis for significant terms was conducted using Tukey's test. When necessary, dependent variable data were log-transformed (%C, %N, C stock, BPCA-C g m<sup>-2</sup>) to meet assumptions of equal variance and normality, which were assessed with Studentized residual diagnostic plots. The null hypothesis, i.e., that the independent factor had no effect or that no linear correlation existed between variables, for all tests was evaluated at  $\alpha < 0.05$ . Analyses were run using SAS 9.4.

## 3 Results

### 3.1 Percent and stocks of C and N in forest floor and soil

Values ranged from 29 % in the forest floor to 0.9 %C in the 5–15 cm soil layer for %C, from 0.8 in forest floor to 0.08 % in the 5–15 cm soil layer for %N, and from 40 in the forest floor to 13 in 5–15 cm soil for C : N. We tested for effects of layer, burn severity, slope and their interactions and found that the main effects were distinct for each response variable (%C, %N and C : N). Effects of burn severity ( $p = 0.002$ ) and layer ( $p < 0.001$ ) on %C could not be independently assessed because the burn by layer interaction was also significant ( $p < 0.001$ , Table S1 in the Supplement). Only layer had an effect on %N ( $p < 0.001$ ), while the C : N ratio was affected by slope ( $p = 0.009$ ), burn intensity ( $p < 0.001$ ), layer ( $p < 0.001$ ) and in interaction ( $p < 0.001$ ).

Post hoc comparisons (Table S2) confirmed expected decreases in %C and %N from forest floor to 5–15 cm soil ( $p < 0.001$  for each successive layer), along with a decreasing C : N from forest floor to 0–5 cm soil ( $p < 0.001$ ) and with no change between 0–5 and 5–15 cm soil ( $p = 0.703$ ). The burn severity by layer interaction term illustrated that the ef-

fects of burn were confined to the forest floor layer for %C and C:N. Within the forest floor layer, unburned sites had greater %C than moderately burned ( $p = 0.009$ ) or highly burned sites ( $p < 0.001$ ), and moderately burned sites also had greater %C than highly burned sites ( $p < 0.001$ ). For the C:N ratio the pattern was the same: C:N was highest at unburned sites and decreased significantly at moderately burned sites ( $p < 0.001$ ) and further still at highly burned sites ( $p < 0.001$ ). Interestingly, slope also had an effect on the C:N. Post hoc comparisons indicated that C:N on 0–5° slopes was lower than 5–15° slopes ( $p = 0.028$ ) and that the C:N on 0–5° slopes was significantly lower than 15–30° slopes ( $p = 0.012$ ), while the 5–15 and 15–30° slopes were not different ( $p = 0.916$ ).

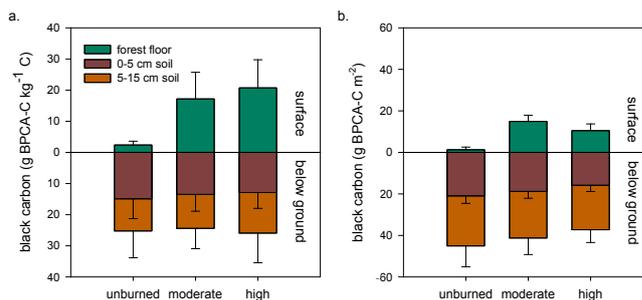
Total C stocks varied considerably between the layers from 3.8 in forest floor to 25.3 tons C hectare<sup>-1</sup> in the 5–15 cm soil layer. The only significant effect on total C stocks was depth ( $p < 0.001$ ), with the forest floor having a smaller C stock than 0–5 and 5–15 cm soil layers ( $p < 0.001$ , for each). Soil bulk density values were not significantly different among any of the study sites (Table S1).

### 3.2 Benzene polycarboxylic acid C in forest floor and soil

We determined BPCA-C both in reference to the amount of carbon and the stock by volume of soil or forest floor and found highly variable amounts of BPCA-C for both metrics. For forest floor, concentration values ranged from 0.09 g kg<sup>-1</sup> C in unburned forest floor to 40.0 g kg<sup>-1</sup> C in highly burned forest floor, and for stocks they range from 0.1 g m<sup>-2</sup> in unburned forest floor to 19.52 g m<sup>-2</sup> in moderately burned forest floor. In soils, concentration ranged from 2.86 g kg<sup>-1</sup> C in moderately burned 0–5 cm soil to 33.83 g kg<sup>-1</sup> C in 5–15 cm highly burned soils, and stocks ranged from 2.92 g m<sup>-2</sup> in highly burned 0–5 cm soils to 96.66 g m<sup>-2</sup> in unburned 5–15 cm soil.

Burn severity and layer were the main effects on the concentration and stock of BPCA-C (Fig. 2, Table S3). Results of a mixed model (slope, burn severity, layer and interactions) indicated that there was no significant effect of slope either independently ( $p = 0.446$ ) or in interaction (slope × burn  $p = 0.191$ , slope × layer  $p = 0.740$ ) on BC concentration. Mean values for BPCA-C stock did decrease with increasing slope in moderately burned forest floor (0–5°:  $18.2 \pm 7.1$ ; 5–15°:  $14.8 \pm 4.7$ ; 15–30°:  $11.8 \pm 4.3$  g m<sup>-2</sup>); however, the trend was not significant due to high variability. The independent effects of burn severity (concentration:  $p = 0.007$ ; stock:  $p = 0.012$ ) and layer (concentration:  $p = 0.610$ ; stock  $p < 0.001$ ) could not be interpreted independently as the interaction of burn severity and layer was also significant (concentration and stock: burn × layer  $p < 0.001$ ).

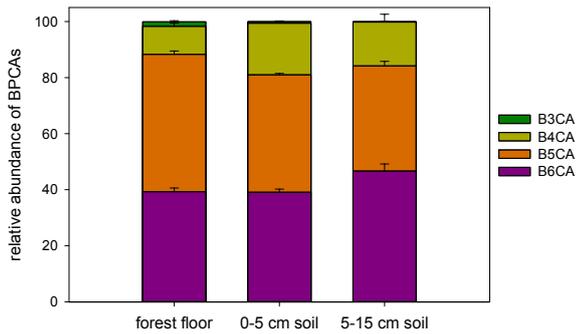
Post hoc comparisons indicated that within the forest floor layer, highly and moderately burned material contained significantly more BPCA-C, both by concentration and stock,



**Figure 2.** Distribution of black carbon in ponderosa pine forest floor in (a) g BPCA-C kg<sup>-1</sup> C and (b) g BPCA-C × m<sup>-2</sup> in forest floor ( $n = 12$ ), 0–5 cm ( $n = 12$ ) and 5–15 cm ( $n = 12$ ) soils, illustrating the significant differences in unburned versus moderately burned forest floor ( $p < 0.001$ ), highly burned forest floor ( $p < 0.001$ ), and unburned forest floor versus 0–5 cm soils ( $p < 0.001$ ) and 5–15 cm soils ( $p < 0.001$ ).

than unburned material (Table S4,  $p < 0.001$  for both). Within the 0–5 and 5–15 cm layers, there was no statistically significant difference in BPCA-C concentration or stock regardless of burn severity. Within unburned layers, 0–5 and 5–15 cm soils had significantly greater amounts of BPCA-C than forest floor, both by concentration ( $p < 0.001$  and  $p = 0.004$ , respectively) and stock ( $p < 0.001$  for both). Within high burn severity, forest floor and soil BPCA-C stocks and concentrations yielded distinct results: the amount of C that was BPCA-C was greater in the forest floor than in 0–5 and 5–15 cm soils ( $p = 0.023$  and  $p = 0.027$ , respectively), whereas the stock of BPCA-C was not significantly different in the high burn among forest floor and soil layers.

We expected that the layer (forest floor, 0–5 and 5–15 cm soil) and burn severity may contribute to the distribution of BPCAs with BC formed at different temperatures (B5CA : B6CA) or by a higher proportion of more condensed C (B6CA : total BPCAs) with increasing soil depth. Overall, the bulk of BPCAs were B5CA and B6CA varieties, together making up approximately 80 % of the total BPCA-C. The B4CAs were the next most abundant (10–20 %), and the B3CAs were less than 3 %. Results from statistical analyses indicated that “layer” was the main effect on the distribution of BPCAs ( $p < 0.001$ , Table S5). Layer also had a significant effect on the ratio of B5CA to B6CA ( $p = 0.002$ ; Table S5, Fig. 4). Post hoc comparisons were used to evaluate the relative abundance of each BPCA by layer: the proportion of B6CA was greater in the 5–15 cm soils than both in the 0–5 cm soils and forest floor layers ( $p < 0.001$ ); B5CA was greater in the forest floor than in 0–5 cm and 5–15 cm soils ( $p < 0.001$  for both) and greater in 0–5 than 5–15 cm soils ( $p = 0.037$ ); B4CA was greater in 0–5 cm soils than in forest floor ( $p < 0.001$ ) and 5–15 cm soils ( $p = 0.002$ ), with no difference in forest floor and 5–15 cm soils ( $p = 0.148$ ). The ratio of B5CA : B6CA decreased with depth due to both decreasing amounts of B5CA and increasing amounts of



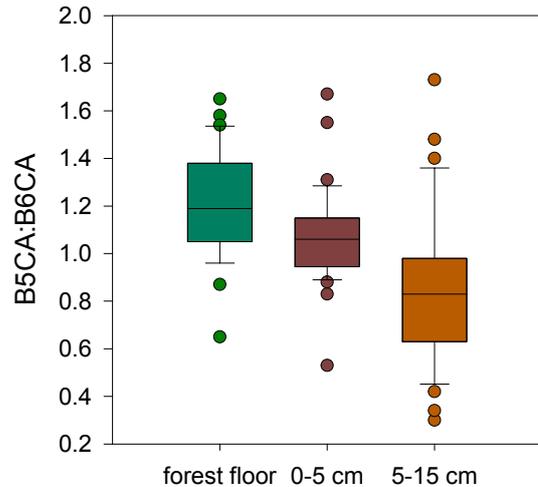
**Figure 3.** Distribution of BPCAs in each layer ( $n = 36$  per layer), illustrating greater relative abundance of B6CA in 5–15 cm soil versus 0–5 cm soil ( $p < 0.001$ ) and forest floor ( $p < 0.001$ ).

B6CA. The B5CA : B6CA ratio was significantly greater in the forest floor than in 5–15 cm soils ( $p = 0.001$ ; Fig. 3, Table S6).

#### 4 Discussion

Our primary objective was to determine the C stocks, BPCA-C stocks and the proportion of C that was BPCA-C in ponderosa pine forest floor and soils following the HPF. BC can account for 1 to 45 % of the soil organic C, depending upon fire return interval (Czimczik et al., 2005; Saiz et al., 2014), ecosystem type, soil mineralogical properties (Preston and Schmidt, 2006) and other factors that influence OC stabilization (Knicker, 2011) as well as on the method used for quantification. Estimates of BC content based on BPCA measurements are generally lower than those made with photo-, chemical- or thermal oxidation-based measurements or with NMR (Preston and Schmidt, 2006). Only a few studies have estimated the amount of BC in forest soils using the BPCA method, with values that range from 10 to 60 g kg<sup>-1</sup> organic C and 0–80 g m<sup>-2</sup> (Czimczik et al., 2003, 2005; Rodionov et al., 2006). Excluding unburned forest floor samples, we found values within this range averaging 14 ( $\pm 7$ ) g BPCA-C kg<sup>-1</sup> C and 19 ( $\pm 5$ ) g BPCA-C m<sup>-2</sup>. It is important to note that BPCAs are markers for BC, and their total amount is estimated to be 2–5 times lower than the amount of BC. This should be taken into consideration when comparing BPCA estimates with BC distribution values in systems that have been assessed with different methods (Brodowski et al., 2005; Glaser et al., 1998; Ziolkowski et al., 2011).

We also aimed to determine how the slope of the landscape and burn severity would influence the amount of BC in forest floor and soil layers following a major wildfire. We found that neither slope nor burn severity had an effect on BC concentration in soils. Interestingly, even the soils from unburned sites had an average BC content of 14 g BPCA-C kg<sup>-1</sup> of C, suggesting a persistent BC pool from past fires. Within the forest floor layer, however, un-



**Figure 4.** Ratio of B5CA to B6CA from 0.2 to 2.0, illustrating an increasing amount of B6CA and decreasing amount of B5CA with increasing soil depth ( $n = 12$  per layer) and a significant difference between forest floor ratio and 5–15 cm ratio ( $p < 0.001$ ).

burned sites contained very low BPCA-C and moderate and highly burned sites contained significantly more, averaging 18 g BPCA-C kg<sup>-1</sup> of OC and suggesting that the majority of the BC remaining on the landscape after the HPF persisted in the forest floor rather than moving into the surface soil 4 months post-fire.

We expected that during the interval between the HPF (June 2013) and sample collection (October 2013), HPF-derived BC would have begun to move off of steeper slopes during post-fire erosion events, resulting in lower BC deposits on steeper slopes. However, we observed consistent BC content across slopes with the HPF-derived BC isolated to the forest floor layer in both highly and moderately burned areas on a per unit C and per square meter basis. Although slope did not contribute to the landscape pattern of BC distribution over the time period of our study, the summer of 2013 was particularly dry with very few high-intensity rain events (Wohl, 2013). Thus, slope may only become a contributing variable to landscape-level post-fire BC distribution when there are precipitation events sufficient to produce significant sediment movement. In addition, steeper slopes generally have increased surface roughness in montane systems constraining overland sediment movement (Wohl, 2013). We qualitatively examined photos of each of the collection sites and noted increased surface roughness in some of the steeper replicates; thus, increased surface roughness is a plausible explanation for similar BPCA-C values on shallow vs. steeper slopes.

The position of our sites in the landscape may have also contributed to the lack of effect of slope on BC distribution. Because our aim was to address slope, rather than position, the sites were not oriented in a consistent up- or downslope manner; thus, some 0–5° sites are located on hilltops and oth-

ers at valley bottoms. In addition, the landscape position influences the location of ponderosa pine through elevational temperature and moisture gradients (Peet, 1981). We focused on the ponderosa pine because it is the dominant vegetation in the drainage, located on a variety of slopes, whereas consideration of hillslope processes would require accounting for the differences in fire properties and BC inputs that would likely result from grass- or shrub-dominated areas (DeBano, 2000).

The only variable that we found responsive to slope was the C:N ratio, which increased with increasing slopes. The constituent %C and %N values were not significantly different by slope, so the pattern was driven by both slight increases in %C and decreases in %N (Table 1). The trend of higher C:N at steeper sites has been noted on the Colorado Plateau (Norton et al., 2003) and was attributed to the accumulation of fresh, plant-derived high-C:N forest floor on steeper slopes in a N-immobilizing environment and the movement of lower-C:N, partially decomposed material, downslope with rain events. Thus over time, steeper slopes do preferentially move material downslope, but this export mechanism did not apply to the BC that was stabilized in soils over time.

Concentrations of post-fire BC have been shown to be highest in the surface of moderately burned soils due to consumption of relict BC content in highly burned areas (Czimczik et al., 2003). However, in our study, on a per unit C basis the amount of BC in surface 0–5 cm soils was not distinguishable across burn intensities ( $\sim 14$  g BPCA-C kg<sup>-1</sup>), while on a per square meter basis, moderately burned material had greater BC content (20 g BPCA-C m<sup>-2</sup>) than unburned material (17 g BPCA-C m<sup>-2</sup>). The cumulative difference between unburned and moderately burned material was driven by low BC content in the forest floor layer at unburned sites. While the highly burned material did not contain significantly less BC than the moderately burned material, it was also not significantly different from unburned material, largely driven by cumulative losses from both the forest floor and 0–5 cm soil BC stocks. Essentially, the stocks of BC at unburned and highly burned sites are the same; they are just distributed differently: the highly burned sites have greater BC stocks in forest floor than soil, and the unburned sites have greater BC stocks in soil than forest floor (Fig. 2).

We were initially surprised to find the same amount of BPCA-C in soils from unburned and burned sites. The BC at unburned sites must be from prior fires, making up a relatively small stock twice the size of the BC found in the forest floor from the HPF. These data suggest that eventually a proportion of the BC produced during the HPF will be introduced into the soils and retained in the ecosystem. Given a fire return interval of  $\sim 70$  years in ponderosa pine forests and a mean residence time for BC stock in soils of approximately 300 years (Hammes et al., 2008; Schmidt et al., 2011), using first-order decay, we calculated that 2.4 g m<sup>-2</sup>, or 17 %, of the HPF-derived BC in forest floor ( $\sim 14$  g m<sup>-2</sup>)

would be transferred to the 0–15 cm soils to maintain a steady-state stock ( $\sim 40$  g m<sup>-2</sup>). This calculation contains a high degree of uncertainty; a greater residence time of BC would result in decreased incorporation, and the reverse would be the case for a shorter residence time; fires with different properties will deposit different amounts of BC on the soil.

The estimate for BC incorporation described above is not meant to be used as a characteristic value of this ecosystem, but instead is meant to illustrate that the bulk of the BC in this system likely moves off the surface, either through incorporation into deeper soils, biotic or abiotic degradation, or export through erosion. BC incorporation at depth via water flow and biotic infiltration processes stimulated by soil fauna has been suggested to be the prime mechanism by which BC is sequestered in the soil (Czimczik and Masiello, 2007), although we would have expected to see some increase in the BC content of surface soils at burned sites if incorporation to deep soil was the dominant mechanism. An additional alternative is the loss of BC through biotic and abiotic degradation, as a proportion of BC is known to be labile (Zimmerman, 2010); however, that proportion is small (Stewart et al., 2013; Zimmerman and Gao, 2013) and other mechanisms are most likely to contribute to major loss pathways. Erosion rates in montane ecosystems post-fire can increase up to 3 orders of magnitude depending on the severity of the fire and the intensity of precipitation (Wagenbrenner and Robichaud, 2014). Erosion has been shown to be important for BC distribution, as previous work has demonstrated that approximately 50 % of BC may be lost through erosion processes (Major et al., 2010; Rumpel et al., 2009). While each of these loss mechanisms – degradation, downward translocation and erosion – may be important for BC distribution in the CLP drainage, preliminary BC data from sediment fences and river banks (Boot et al., 2014), along with a report on dissolved and particulate BC export (Wagner et al., 2015), suggests that erosion may be a dominant source of BC loss in this system.

Our third objective was to describe the distribution of BPCAs within forest floor and soil layers to determine whether the molecular structure of BC was characteristic by layer or influenced by burn severity. Recently, Wiedemeier and others confirmed that the proportion of B6CAs relative to the total BPCAs measured directly correlated with both the degree of condensation and the aromaticity of chars; thus, we used the relative abundance of B6CA: total BPCA to describe the molecular features of BC (Fig. 3). We found that B6CA relative abundance was greater in the 5–15 cm soils relative to forest floor, suggesting that more condensed BC is present in deeper soils at these sites; there was no effect of burn severity on BPCA abundances. The relative abundance of B6CA has also been associated with the highest heat treatment temperature (HTT), correlating increasing HTT with increasing condensation (Schneider et al., 2013).

**Table 1.** Site characteristics (%C, %N, C : N, C stock) of forest floor, 0–5 cm soil and 5–15 cm soil classified by burn severity and slope. Mean values reported with standard errors in parentheses ( $n = 4$ ).

Layer	Burn severity	Slope (degrees)	%C	%N	C : N (tC × ha <sup>-1</sup> )	C stock
Forest floor	Unburned	0 to 5	27.31 (7.72)	0.72 (0.18)	37.8 (2.4)	6.6 (3.9)
		5 to 15	23.39 (5.75)	0.73 (0.10)	40.5 (4.2)	5.7 (1.5)
		15 to 30	29.13 (5.81)	0.71 (0.11)	40.2 (2.1)	6.0 (1.2)
	Moderate	0 to 5	15.68 (1.44)	0.70 (0.13)	23.5 (2.5)	10.4 (2.4)
		5 to 15	22.35 (7.43)	0.80 (0.15)	26.4 (3.8)	10.9 (3.6)
		15 to 30	17.51 (2.97)	0.62 (0.09)	28.1 (1.8)	6.0 (2.2)
	High	0 to 5	7.07 (2.18)	0.43 (0.13)	16.6 (0.2)	3.8 (1.1)
		5 to 15	13.98 (3.09)	0.68 (0.12)	20.6 (2.1)	7.5 (4.6)
		15 to 30	9.23 (2.31)	0.44 (0.10)	21.4 (3.7)	5.4 (1.9)
0–5 cm soil	Unburned	0 to 5	2.89 (1.38)	0.18 (0.06)	14.5 (2.7)	14.1 (6.3)
		5 to 15	2.75 (0.43)	0.17 (0.03)	16.1 (1.1)	15.1 (1.8)
		15 to 30	2.99 (0.56)	0.17 (0.03)	17.9 (1.5)	13.3 (3.2)
	Moderate	0 to 5	2.42 (0.38)	0.16 (0.02)	15.0 (0.2)	11.4 (2.1)
		5 to 15	3.62 (0.68)	0.19 (0.04)	19.4 (2.3)	14.1 (2.8)
		15 to 30	3.23 (0.26)	0.17 (0.01)	18.7 (1.6)	17.7 (2.1)
	High	0 to 5	2.09 (0.25)	0.14 (0.02)	14.9 (0.7)	9.0 (1.5)
		5 to 15	2.25 (0.37)	0.14 (0.03)	16.5 (1.6)	11.7 (1.7)
		15 to 30	2.63 (0.24)	0.16 (0.02)	16.4 (1.0)	14.4 (2.9)
5–15 cm soil	Unburned	0 to 5	1.82 (1.19)	0.12 (0.06)	13.2 (2.4)	17.8 (9.4)
		5 to 15	1.87 (0.53)	0.11 (0.04)	17.7 (1.6)	25.3 (9.1)
		15 to 30	1.47 (0.50)	0.08 (0.03)	18.5 (2.9)	13.5 (3.8)
	Moderate	0 to 5	1.61 (0.35)	0.10 (0.02)	17.0 (2.0)	17.4 (0.3)
		5 to 15	0.97 (0.21)	0.06 (0.01)	16.5 (1.8)	16.3 (8.5)
		15 to 30	1.21 (0.19)	0.08 (0.02)	15.5 (1.2)	15.8 (5.6)
	High	0 to 5	1.29 (0.16)	0.09 (0.01)	15.4 (1.1)	14.3 (5.4)
		5 to 15	1.20 (0.15)	0.08 (0.01)	14.7 (1.2)	13.0 (2.0)
		15 to 30	1.48 (0.32)	0.10 (0.02)	14.9 (0.7)	13.9 (3.3)

Forest fire temperatures are difficult to determine and can range from approximately 1000 °C in the canopy to a maximum of 850 °C at the surface, averaging approximately 300, and rarely exceed 150 °C at 5 cm in the mineral soil (DeBano, 2000; Wolf et al., 2013). While it is tempting to derive HTT from BC deposited on the soil surface following the fire, it must be noted that surface and soil BC is likely to be a pool integrated across sources that were pyrolyzed over the range of fire temperatures. The amount of B6CA has been shown to correlate directly with HTT for bark and wood materials, yet no clear relationship exists between B6CA concentrations and the temperature of charring for pine-needle- or leaf-derived chars (Schneider et al., 2010, 2013). Information on HTT from B6CA alone can be bolstered by also using the ratio of B5CA : B6CA, which has a significant inverse linear relationship with combustion temperature. Natural chars range from B5CA : B6CA values 1.3 to 1.9 for cooler burning forest fires (~ 300 °C), 0.8 to 1.4 for hotter

grass and shrub fires (~ 500 °C) and < 0.8 for the hottest burning domestic fires (800 °C; Wolf et al., 2013). In HPF impacted areas, the forest floor had a B5CA : B6CA ratio of 1.2, which would be at the border between grass or shrub and forest fires and yield an integrated predicted temperature of around 400 °C, whereas the B5CA : B6CA ratio for 5–15 cm soils was significantly lower, averaging 0.8 and thus corresponding to a higher combustion temperature of approximately 600 °C, which matches well with the temperatures that would be predicted from the B6CA content alone. Other studies have suggested that the pattern of BPCAs may be informative for determining the amount of processing by microorganisms (Rodionov et al., 2010), although these correlations have not been empirically validated and abiotic degradation, such as preferential leaching of less condensed forms of BC, would also shift the relative abundance of the BPCA pattern (Abiven et al., 2011). Thus, the greater B6CA content and decreasing B5CA : B6CA ratio in deeper soils from

our study may represent either BC derived from greater average HTT in past events, selective removal of less condensed forms of BC through preferential solubilization (Abiven et al., 2011) or other biotic or abiotic degradation of less condensed forms of BC.

## 5 Conclusions

The distribution of BC on a landscape will influence how an ecosystem recovers following a wildfire. Although BC is generally considered nearly biologically inert, its impact on soil physical properties may alter biogeochemical cycling. For example, BC amendments in agricultural systems (as biochar) have been shown to change water-holding capacity and nutrient retention (Lehmann, 2007); thus, its persistence in post-fire soils may be beneficial to, or otherwise alter, vegetation recovery dynamics. BC has also been shown to enhance the growth of microorganisms, potentially increasing the accumulation of new SOM (Bird et al., 1999). In addition to altering post-fire recovery dynamics, the movement of BC following wildfire also has implications for water quality, including municipal water treatment techniques as well as reductions in primary productivity in streams and sediments through increased sediment load (Wood and Armitage, 1997). Our results suggest the vast majority of HPF-derived BC deposited on the landscape persisted in the forest floor 4 months post-burn, regardless of slope, and was formed at an average temperature of approximately 400 °C. Stocks of BC in this montane ecosystem were relatively small and were not altered by the HPF; thus, subsequent distribution will be governed by modes of BC loss likely related to erosion of the forest floor layer and may also include transport into the soils via dissolution and translocation as well as biotic or abiotic degradation.

**The Supplement related to this article is available online at doi:10.5194/bg-12-3029-2015-supplement.**

*Author contributions.* M. F. Cotrufo and K. Paustian designed the experiment. M. Haddix coordinated and executed field sampling and site characteristic analyses. C. M. Boot and M. L. Haddix performed BPCA analyses and C. M. Boot prepared the manuscript.

*Acknowledgements.* We would like to thank John Norman for site selection assistance, Tara Baker, Geoffrey Bedrosian, Jake Betzen, Bryan Brown, Joey E'Silva, Claire Freeman, Michael Jurich, Daniel Kovar, Robert Murphy, Halle Poppaw, and Allison Reser for sample collection and processing, Amy Swan for assistance in mapping and site selection, Shinichi Asao for discussion on MRT, and Ann Hess for assistance with statistical analyses.

We would also like to acknowledge the method implementation assistance of D. Wiedemeier and constructive feedback provided by three anonymous reviewers as well as D. Wiedemeier and U. Hanke. Funding was provided through NSF-RAPID #1261383 and the Cotrufo-Hoppess fund for soil ecology research. Analyses were completed at EcoCore Analytical Services, Natural Resource Ecology Laboratory at Colorado State University (<http://ecocore.nrel.colostate.edu>).

Edited by: K. Guan

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