Biogeosciences Discuss., 11, 16799–16824, 2014
www.biogeosciences-discuss.net/11/16799/2014/
doi:10.5194/bgd-11-16799-2014

Biogeosciences Discussions
Open Access

Distribution of black carbon in Ponderosa pine litter and soils following the High Park wildfire

C. M. Boot[1], **M. Haddix**[1], **K. Paustian**[1,2], **and M. F. Cotrufo**[1,2]

[1]Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO 80523, USA
[2]Department of Soil and Crop Sciences, Colorado State University, Fort Collins, CO 80523, USA

Received: 12 September 2014 – Accepted: 18 November 2014 – Published: 5 December 2014

Correspondence to: C. M. Boot (claudia.boot@colostate.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Black carbon (BC), the heterogeneous product of burned biomass, is a critical component in the global carbon cycle, yet timescales and mechanisms for incorporation into the soil profile are not well understood. The High Park Fire, which took place in northwestern Colorado in the summer of 2012, provided an opportunity to study the effects of both fire intenstiy and geomorphology on properties of carbon (C), nitrogen (N), and BC in the Cache La Poudre River drainage. We sampled montane Ponderosa pine litter, 0–5 cm soils, and 5–15 cm soils four months post-fire in order to examine the effects of slope and burn intensity on %C, C stocks, %N and black carbon (g kg^{-1} C, and g m^{-2}). We developed and implemented 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 black carbon content or stocks. BC content was greatest in the litter in burned sites (19 g kg^{-1} C), while BC stocks were greatest in the 5–15 cm subsurface soils (23 g m^{-2}). At the time of sampling, none of the BC deposited on the land surface post-fire had been incorporated into to either the 0–5 cm or 5–15 cm soil layers. The ratio of B5CA : B6CA (less condensed to more condensed BC) indicated there was significantly more older, more processed BC at depth. 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 transported off the surface through erosion events. Future work examining mechanisms for BC transport 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 arguably the least understood component of the terrestrial C cycle. Every year, fire burns approximately 10–15 × 10^6 ha of boreal and temperate forest and

BGD
11, 16799–16824, 2014

more than 500×10^6 ha of tropical and subtropical forests and savannas (Goldammer and Crutzen, 1993; Knicker, 2011), in 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). Thus 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), and thus BC stocks are strongly dependent on surface topography and soil physical-chemical environment (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). BC particles are composed of a refractory, aromatic core and a reactive, oxidized patina (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), 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 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 and geomorphology. The shape of a landscape and propensity for erosion vs. deposition is dependent upon several variables including bedrock com-

BGD
11, 16799–16824, 2014

position, slope, elevational gradients in temperature and precipitation, and disturbance history such as the frequency of wildfires. While the strong relationship between geomorphology and soil erosion/sediment transport is fairly well understood (Slater and Carleton, 1938; Ritchie and McCarty, 2003), the relationship between soil erosion and fate of different components of SOM that are eroded, including BC, are relatively unknown (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 (Masiello, 2004; Hammes et al., 2007). Visual counts of charcoal, resistance to oxidation methods, nuclear magnetic resonance spectroscopy (NMR) and the quantification of BC-specific molecular biomarkers (e.g., benzene polycarboxylic acids (BPCAs)) have each been employed for 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 information about BC quality related to its degree of aromatic condensation, derived from fire temperature and age (Schneider et al., 2010, 2013; 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 9–24 June, 2012, the High Park fire 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 litter and soils

BGD
11, 16799–16824, 2014

following the High Park Fire; 2. examine the effects of burn intensity and landscape slope on soil C : N ratio and proportion of BC; and 3. use the distribution of individual BPCAs to understand the age and degree of processing of BC through the soil profile. We expected that BPCA stocks would be the greatest in highly burned sites, followed by moderate, then unburned sites, and that the slope of the hill side would have the opposite effect, with lowest BPCA stocks on the steepest slopes, and greatest BC stocks on shallow slopes. We anticipated that BPC-A, C, and N would be greater in litter than in soils, and that soil C stocks would be diminished in highly burned surface soils due to combustion during fire. We also expected that the BC age and degree of processing would increase with depth.

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 menzieii*) and also includes aspen (*Populus termuloides*), Rocky Mountain Juniper (*Juniperus scopulorum*), lodgepole pine (*Pinus contorta*) and other species (Veblen and Donnegan, 2005). Soils in the montane forests are cryoboralfs and 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 lightening strike ignition (Veblen and Donnegan, 2005). A lightening 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.

BGD
11, 16799–16824, 2014

Our study was a fully factorial, randomized block design with four replicate blocks for all treatments plots, including three levels of burn intensity (unburned, moderate burn, high burn) and three slopes (0–5, 5–15 and 15–30°), for a total of 36 plots. 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 intensity 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. Moderate burn areas had ground fire and some crown scorch, but crowns did not burn and at least some needles remained on the trees. Unburned areas had no evidence of ground fire and no evidence of burned material on the ground surface.

2.2 Litter and soil collection

Soil and litter samples were collected between October and November of 2012. At each of the 36 experimental plots, litter and soils were collected from within a 20 cm × 20 cm wooden frame, and frame GPS coordinates recorded. The litter layer was sampled first and then the soil excavated with the help of a hand shovel separately for the 0–5 cm and 5–15 cm depth. Due to the high surface variability, 4 additional litter samples and 3 surface (0–5 cm) soil samples were collected at each site, positioning the frame orthogonally to a distance of 2.5 m from the original position. All litter 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. During excavation, if the majority of a rock resided inside the frame that rock was collected, if the majority of a rock was outside the frame the rock was left in place and the soil was excavated around the rock. Thin nylon fabric was used to line the pit and

BGD
11, 16799–16824, 2014

millet was added to the pit until level with the top of the excavation frame. The volume of the millet was determined with a graduated cylinder. The volume for the 0–5 cm depth was the volume of the millet that filled the entire 0–5 cm depth, with the volume of the frame thickness subtracted. The volume of the 5–15 cm depth was the volume of the millet the filled the entire 0–15 cm depth with the volume of the entire 0–5 cm depth subtracted. Soil and plant samples were transported to the lab and stored at 4 °C until processing.

2.3 Litter and soil pretreatment and elemental analyses

In the laboratory, litter samples were weighed field-moist and a subsample of each was dried at 105 °C for 48 h for dry weight correction. Litter samples were then air-dried and another subsample taken and heated in a muffle furnace at 600 °C for 12 h to correct litter dry weight for ash content. All remaining air-dried litter 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. The soil was then 8 mm sieved and all rocks and roots not passing through the sieve were removed and weighed. The soil was then air-dried and a subsample taken for 2 mm sieving and any rocks and roots not passing through the sieve were removed and weighed. After 2 mm sieving, a subsample was taken, finely ground and dried overnight at 105 °C. 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. All the ground dry litter 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.

BGD
11, 16799–16824, 2014

2.4 BPCA analyses

Black C was determined on all litter and soil samples using high performance liquid chromatography (HPLC) equipped with a photo diode array detector to quantify benzene polycarboxylic acids (BPCA) as described by (Wiedemeier et al., 2013). For the BPCA analysis, 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 reference 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 re-dissolved in HPLC grade water. The re-dissolved solution containing the BPCAs was separated with a reversed stationary phase column (Waters X-Bridge C18, 3.5 µm particle size, 2.1 mm × 150 mm) using a gradient method consisting of mobile phase A: HPLC grade water with 25 mL L^{-1} 85 % orthophosphoric acid buffered with monosodium phosphate to pH 1.2, and mobile phase B: acetonitrile. Gradient separation was 5 min 0.5 % mobile phase B, at 0.2 mL/min, 5 to 25.9 min 30 % mobile phase B, 25.9 to 26 min, 95 % mobile phase B followed by column re-equilibration. Individual BPCAs were quantified with using a 5 point calibration from standard solutions of benzenetricarboxylic acids (1,2,3-B3CA/hemimellitic acid, 1,2,4-B3CA/trimellitic acid, 1,3,5-B3CA/trimesic acid), benzenetetracarboxylic acid (1,2,4,5-B4CA/pyromellictic acid), benzenepentacarboxylic acid (B5CA), and benzenehexacarboxylic acid (B6CA/mellitic acid). The B4CA standards that are not commercially available (1,2,3,4-B4CA/prehenitic acid, and 1,2,3,5-B4CA/mellophanic acid) were identified by their ultraviolet adsorption spectra and quantified using the calibration for 1,2,4,5-B4CA (Yarnes et al., 2011). The BPCA method was validated by evaluating an unburned field soil from our site that was mixed with a laboratory produced biochar at 5, 20 and 50 % soil weight.

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 (Ziolkowski

BGD
11, 16799–16824, 2014

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

Carbon and N stocks in the litter and soil layers were calculated by multiplying the %C along with the bulk density in the soil layers and the biomass per m^2 in the litter layer. The effect of layer (litter, 0–5 cm soil, 5–15 cm soil), slope (0–5°, 5–15°, 15–30°) and burn intensity (unburned, moderate burn, high burn) on each response variable (soil C, soil N, and BPCA C stock, and BPCA C as a proportion of total C) was compared using three-way analysis of variance (ANOVA). The differences in the distribution of BPCAs (B4CA, B5CA and B6CA) among the soil layers and burn intensities were analyzed using two-way ANOVA. When necessary, dependent variable data were log-transformed (%C, %N, C stock, BPCA-C $g\,m^{-2}$) to meet assumptions of equal variance and normality. Linear regression for BPCA method validation was evaluated using Pearson's R. The null hypothesis, that the independent factor had no effect, or that no linear correlation existed between variables, for all tests was evaluated at $\alpha < 0.05$. ANOVA and regression analyses were run using SigmaPlot 12.5 (Systat Software, San Jose, CA).

3 Results

3.1 Percent and stocks of C and N in litter and soil

Values for %C ranged from 29 % in the litter to 0.9 % C in the 5–15 cm soil layer, for %N from 0.8 % in litter to 0.08 % in the 5–15 cm soil layer, and for C : N from 40 in the litter to 13 in 5–15 cm soil. We tested for effects of layer, burn intensity and slope and found that the main effects were distinct for each response variable (%C, %N and C : N). The burn intensity and layer affected %C ($p < 0.001$ for both), and there was a burn × layer interaction ($p < 0.001$). Only layer had an effect on %N ($p < 0.001$), while the C : N ratio

BGD
11, 16799–16824, 2014

was affected by slope ($p = 0.022$), burn intensity ($p < 0.001$), layer ($p < 0.001$) and the burn layer interaction ($p < 0.001$ for each).

Post hoc comparisons confirmed expected decreases in %C and %N from litter to 5–15 cm soil ($p < 0.001$ for each successive layer), along with a decreasing C : N from litter to 0–5 cm soil ($p < 0.001$) and with no change between 0–5 cm and 5–15 cm soil ($p = 0.501$). The burn intensity by layer interaction term illustrated that the effect of burn were confined to the litter layer for %C and C : N. Within the litter layer unburned sites had greater %C than moderately burned ($p = 0.024$) 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 widest in unburned sites which 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 marginally lower than 5–15° slopes ($p = 0.051$) and the C : N on 0–5° slopes was significantly lower than 15–30° slopes ($p = 0.031$), while the 5–15 and 15–30° slopes were not different ($p = 0.722$).

Total C stocks varied considerably between the layers from 3.8 in litter to 25.3 tons C per hectare in the 5–15 cm soil layer. Using a three-way ANOVA to evaluate effects of layer, burn intensity and slope, the only significant effect on total C stocks was depth ($p < 0.001$) with the litter having the smaller C stocks than 0–5 cm 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.

3.2 BPCA Method Validation

The BPCA method validation with biochar-amended soils generated a linear relationship among the samples (BPCA – $C = -1.506 + (0.89 \times \%\ \text{char})$, $r^2 = 0.94$, $p < 0.001$). The coefficients of variation at different amendment levels were 0.05 at 5 % amendment, 0.07 at 20 % amendment, and 0.19 at 50 % amendment. The majority of BPCA-C values in our field study were below the 5 % amendment, thus we concluded the

BGD
11, 16799–16824, 2014

method was robust for quantifying BC and progressed with field-based sample collections.

3.3 Benzene polycarboxylic acid-C in litter and soil

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

Burn intensity and layer were the main effects on the concentration and stock of BPCA-C (Fig. 2, Table S3). Results of a three way ANOVA (slope, burn intensity and layer) indicated that there was no significant effect of slope either independently ($p = 0.357$) or in interaction (slope x burn $p = 0.223$, slope x layer $p = 0.724$). Values for BPCA-C stock did decrease with increasing slope in moderately burned litter (0–5 °: 18.2 ± 7.1 g m^{-2}; 5–15 °: 14.8 ± 4.7 g m^{-2}, 15–30 °: 11.8 ± 4.3 g m^{-2}), however the trend was not significant. The independent effects of burn intensity (concentration: $p = 0.007$, stock: $p = 0.012$), and layer (concentration: $p = 0.541$, stock $p < 0.001$) could not be interpreted as the interaction of burn intensity and layer was also significant (concentration and stock: burn x layer $p < 0.001$).

Post hoc comparisons indicated that within the litter layer, high and moderately burned material contained significantly more BPCA-C, both by concentration and stock, 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 intensity. Within unburned layers, 0–5 and 5–15 cm soils had significantly greater amounts of BPCA-C than litter, both by concentration ($p < 0.001$, $p = 0.003$, respectively) and stock ($p < 0.001$ for both). Within high burn intensity, lit-

BGD
11, 16799–16824, 2014

ter and soil BPCA-C stocks and concentrations yielded distinct results: the amount of OC that was BPCA-C was greater in the litter than 0–5 and 5–15 cm soils ($p = 0.028$, $p = 0.022$, respectively), whereas the stock of BPCA-C was not significantly different in the high burn among litter and soil layers.

We expected that the layer (litter, 0–5 cm soil, 5–15 cm soil) and burn intensity may contribute to the distribution of BPCA biomarkers (Rodionov et al., 2006) with older, more processed BC indicated by a higher proportion of more condensed C (B5CA, B6CA) with increasing soil depth. Overall, the bulk of BPCAs were B5CA and B6CA varieties, together making more than 80 % of the total BPCA-C. The B4CAs were the next most abundant (10–20 %) and the B3CAs were less then 3 %. Results from statistical analyses indicated that "layer" was the main effect on the distribution of BPCAs (Table S5, Fig. 3), as well as on the ratio of B5CA to B6CA, (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 soil than both 0–5 cm soil and litter layers ($p < 0.001$); B5CA was greater in the litter than 0–5 cm soil and 5–15 cm soils ($p < 0.001$ for both), and greater in 0–5 cm soils than 5–15 cm soils ($p = 0.024$); B4CA was greater in 0–5 cm soil than in litter ($p < 0.001$), and 5–15 cm soil ($p = 0.002$), with no difference in litter and 5–15 cm soil ($p = 0.073$). The ratio of B5CA : B6CA decreased with depth due to both decreasing amounts of B5CA and increasing amounts of B6CA. The B5CA : B6CA ratio was not significantly different between litter and 0–5 cm soils ($p = 0.066$), but the ratio was significantly greater in litter and 0–5 cm soils than in 5–15 cm soils ($p < 0.01$ for both).

4 Discussion

Our primary objective was to determine the C and BPCA-C stocks, and the proportion of C that was BPCA-C in ponderosa pine litter and soils following the High Park fire. BC can account for 1 to 45 % of the soil organic C depending upon fire return interval (Saiz et al., 2014; Czimczik et al., 2005), ecosystem type, soil mineralogical proper-

BGD
11, 16799–16824, 2014

ties (Preston and Schmidt, 2006) other factors that influence OC stabilization (Knicker, 2011), as well as the method used for quantification. Estimates of BC content based on BPCA-measurements are generally lower than those made with chemical- thermal- or photo-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 10 to 60 g kg^{-1} organic C and 0–80 g m^{-2} (Czimczik et al., 2003, 2005; Rodionov et al., 2006). Excluding unburned litter samples, we found values within this range, averaging 14 (±7) g BPCA-C kg^{-1} C, and 19 (±5) g BPCA-C m^{-2}.

We also aimed to determine how the slope of the landscape and burn intensity would influence the amount of BC in litter and soil layers following a major wildfire. We found that neither slope nor burn intensity had an effect on BC concentration in soil. Interestingly, even the soils from unburned sites had an average BC content of 14 g BPCA-C kg^{-1} of C, suggesting persistent pools from past fires. Within the litter layer, however, unburned sites contained very low BPCA-C and moderate and highly burned sites contained significantly more, averaging 18 g BPCA-C per kg of OC suggesting that the majority of the BC remaining on the landscape persisted in the litter rather than moving into the surface soil four 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 litter layer in both highly and moderately burned areas on a per kg C and per m^2 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 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 col-

BGD
11, 16799–16824, 2014

lection sites and noted increased surface roughness in some of the steeper replicates, thus increased surface roughness is also a plausible explanation for similar BPCA-C values on shallow vs. steeper slopes.

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 must be 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 litter 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 does 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 (Czimczik et al., 2003) due to consumption of relict BC content in highly burned areas. In our study, on a per kg C basis the amount of BC in surface 0–5 cm soils was identical across burn intensities, while on a per m^2 basis, moderately burned material had greater BC content than unburned material. The cumulative difference between unburned and moderately burned material was driven by low BC content in the litter 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 litter and 0–5 cm soil BC stocks. Essentially, the stocks of BC in unburned and highly burned sites are the same, they are just distributed differently: the highly burned sites have greater BC stocks in litter than soil, and the unburned sites have greater BC stocks in soil than litter (Fig. 2).

We were initially surprised to find the same amount of BPCA-C in soils from unburned and burned sites. The BC in unburned sites must be from prior fires, making up a relatively small stock twice the size of BC found in the litter from the HPF. These

BGD
11, 16799–16824, 2014

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 ~ 70 years in Ponderosa 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^{-2}, or 17 % of the HPF fire-derived BC in litter (~ 14 g m^{-2}) would be transferred to the 0–15 cm soil to maintain a steady state stock (~ 40 g m^{-2}). This calculation contains a high degree of uncertainty; a greater residence time would result in decreased incorporation, and the reverse for a shorter residence time. These values are not meant to be used as characteristic value for this ecosystem, but instead are meant to illustrate that the bulk of the BC in this system likely moves off the landscape through surface runoff. Previous work has demonstrated up to 53 % of BC was lost through runoff (Major et al., 2010). Alternatively, BC incorporation at depth via water flow and biotic infiltration processes, 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 surface soils if incorporation to deep soil was the dominant mechanism. Each of these mechanisms for transport could be important for BC distribution in the CLP watershed and will be largely dependent on climatic variation following wildfires.

Our third objective was to describe the distribution of BPCA biomarkers within litter and soil layers to determine if the molecular structure of BC is altered with increasing depth or burn intensity. The distribution of the BPCA biomarkers with increasing amounts of B6CA and a decreasing ratio of B5CA : B6CA with depth suggests that greater amounts of larger, more condensed BC, that has undergone more processing, is present in deeper soils. The decreasing B5CA : B6CA ratio with increasing depth suggested that the BC in deeper soils is older, and more highly processed than material from the surface (Rodionov et al., 2006). The largest difference between the litter and the 0–5 cm soil is a decrease in the proportion of B5CA, and an increase in the proportion of B4CA. Similarly, between the 0–5 cm soils and the 5–15 cm soils there are losses of the B4CA, a relative decrease in the B5CA and an increase in the B6CA. This

BGD
11, 16799–16824, 2014

dynamic pattern suggests that the least condensed forms of BC are lost first (e.g. B4CA in litter) (Abiven et al., 2011), resulting in increasing abundance of more condensed forms of BC (e.g. produces B5CA upon oxidation) and losses of less condensed forms of BC through oxidation or leaching (Ziolkowski et al., 2011).

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 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 litter layer four-months post burn, and that its subsequent distribution will be governed by erosion of the litter layer and transport into the soils via dissolution and translocation.

5 Conclusions

We found that the majority of the BC deposited following the fire remained in the litter layer and was equal in moderate and highly burned sites.

The Supplement related to this article is available online at doi:10.5194/bgd-11-16799-2014-supplement.

BGD
11, 16799–16824, 2014

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 developed the BPCA method, performed BPCA analyses and 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, Amy Swan for assistance with GIS mapping and processing and Shinichi Asao for discussion on MRT. 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).

References

Abiven, S., Hengartner, P., Schneider, M. P. W., Singh, N., and Schmidt, M. W. I.: Pyrogenic carbon soluble fraction is larger and more aromatic in aged charcoal than in fresh charcoal, Soil Biol. Biochem., 43, 1615–1617, doi:10.1016/j.soilbio.2011.03.027, 2011.

Baldock, J. A. and Smernik, R. J.: Chemical composition and bioavailability of thermally, altered Pinus resinosa (Red Pine) wood, Org. Geochem., 33, 1093–1109, 2002.

Bird, M. I., Moyo, C., Veenendaal, E. M., Lloyd, J., and Frost, P.: Stability of elemental carbon in a savanna soil, Global Biogeochem. Cy., 13, 923–932, doi:10.1029/1999gb900067, 1999.

Birkeland, P. W., Shroba, R. R., Burns, S. F., Price, A. B., and Tonkin, P. J.: Integrating soils and geomorphology in mountains-an example from the Front Range of Colorado, Geomorphology, 55, 329–344, 2003.

Cheng, C. H., Lehmann, J., Thies, J. E., Burton, S. D., and Engelhard, M. H.: Oxidation of black carbon by biotic and abiotic processes, Org. Geochem., 37, 1477–1488, doi:10.1016/j.orggeochem.2006.06.022, 2006.

Cheng, C. H., Lehmann, J., and Engelhard, M. H.: Natural oxidation of black carbon in soils: changes in molecular form and surface charge along a climosequence, Geochim. Cosmochim. Ac., 72, 1598–1610, doi:10.1016/j.gca.2008.01.010, 2008.

Christensen, B. T.: Carbon in primary and secondary organomineral complexes, in: Structure and Organic Matter Storage in Agricultural Soils, edited by: Carter, M. R. and Stewart, B. A., CRC Press, Inc, Boca Raton, FL, 97–165, 1996.

BGD
11, 16799–16824, 2014

Cusack, D. F., Chadwick, O. A., Hockaday, W. C., and Vitousek, P. M.: Mineralogical controls on soil black carbon preservation, Global Biogeochem. Cy., 26, GB2019, doi:10.1029/2011gb004109, 2012.

Czimczik, C. I., Preston, C. M., Schmidt, M. W. I., and Schulze, E.-D.: How surface fire in Siberian Scots pine forests affects soil organic carbon in the forest floor: stocks, molecular structure, and conversion to black carbon (charcoal), Global Biogeochem. Cy., 17, 1020, doi:10.1029/2002gb001956, 2003.

Czimczik, C. I., Schmidt, M. W. I., and Schulze, E. D.: Effects of increasing fire frequency on black carbon and organic matter in Podzols of Siberian Scots pine forests, Eur. J. Soil Sci., 56, 417–428, doi:10.1111/j.1365-2389.2004.00665.x, 2005.

Czimczik, C. I. and Masiello, C. A.: Controls on black carbon storage in soils, Global Biogeochem. Cy., 21, GB3005, doi:10.1029/2006gb002798, 2007.

Foereid, B., Lehmann, J., and Major, J.: Modeling black carbon degradation and movement in soil, Plant Soil, 345, 223–236, doi:10.1007/s11104-011-0773-3, 2011.

Forbes, M. S., Raison, R. J., and Skjemstad, J. O.: Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems, Sci. Total Environ., 370, 190–206, doi:10.1016/j.scitotenv.2006.06.007, 2006.

Goldammer, J. G. and Crutzen, P. J.: Fire in the environment: scientific rationale and summary of results of the Dahlem Workshop, in: Fire in the Environment: the Ecological, Atmospheric and Climatic Importance, edited by: Crutzen, P. J. and Goldammer, J. G., John Wiley & Sons, Toronto, 1–14, 1993.

Hammes, K., Schmidt, M. W. I., Smernik, R. J., Currie, L. A., Ball, W. P., Nguyen, T. H., Louchouarn, P., Houel, S., Gustafsson, Ö., Elmquist, M., Cornelissen, G., Skjemstad, J. O., Masiello, C. A., Song, J., Peng, P. a., Mitra, S., Dunn, J. C., Hatcher, P. G., Hockaday, W. C., Smith, D. M., Hartkopf-Fröder, C., Böhmer, A., Lüer, B., Huebert, B. J., Amelung, W., Brodowski, S., Huang, L., Zhang, W., Gschwend, P. M., Flores-Cervantes, D. X., Largeau, C., Rouzaud, J.-N., Rumpel, C., Guggenberger, G., Kaiser, K., Rodionov, A., Gonzalez-Vila, F. J., Gonzalez-Perez, J. A., de la Rosa, J. M., Manning, D. A. C., López-Capél, E., and Ding, L.: Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere, Global Biogeochem. Cy., 21, GB3016, doi:10.1029/2006gb002914, 2007.

BGD
11, 16799–16824, 2014

Hammes, K., Torn, M. S., Lapenas, A. G., and Schmidt, M. W. I.: Centennial black carbon turnover observed in a Russian steppe soil, Biogeosciences, 5, 1339–1350, doi:10.5194/bg-5-1339-2008, 2008.
Knicker, H.: Pyrogenic organic matter in soil: its origin and occurrence, its chemistry and survival in soil environments, Quatern. Int., 243, 251–263, doi:10.1016/j.quaint.2011.02.037, 2011.
Lehmann, J., Liang, B. Q., Solomon, D., Lerotic, M., Luizao, F., Kinyangi, J., Schafer, T., Wirick, S., and Jacobsen, C.: Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy for mapping nano-scale distribution of organic carbon forms in soil: application to black carbon particles, Global Biogeochem. Cy., 19, Gb1013 doi:10.1029/2004gb002435, 2005.
Lehmann, J.: Bio-energy in the black, Front. Ecol. Environ., 5, 381–387, doi:10.1890/1540-9295(2007)5[381:BITB]2.0.CO;2, 2007.
Major, J., Lehmann, J., Rondon, M., and Goodale, C.: Fate of soil-applied black carbon: downward migration, leaching and soil respiration, Glob. Change Biol., 16, 1366–1379, doi:10.1111/J.1365-2486.2009.02044.X, 2010.
Masiello, C. A.: New directions in black carbon Org. Geochem., Mar. Chem., 92, 201–213, doi:10.1016/j.marchem.2004.06.043, 2004.
McBeath, A. V. and Smernik, R. J.: Variation in the degree of aromatic condensation of chars, Org. Geochem., 40, 1161–1168, doi:10.1016/j.orggeochem.2009.09.006, 2009.
Norton, J. B., Sandor, J. A., and White, C. S.: Hillslope soils and organic matter dynamics within a Native American agroecosystem on the Colorado Plateau, Soil Sci. Soc. Am. J., 67, 225–234, 2003.
Page-Dumroese, D. S., Jurgensen, M. F., Brown, R. E., and Mroz, G. D.: Comparison of methods for determining bulk densities of rocky forest soils, Soil Sci. Soc. Am. J., 63, 379–383, 1999.
Peet, R. K.: Forest vegetation of the colorado front range – composition and dynamics, Vegetatio, 45, 3–75, 1981.
Preston, C. M. and Schmidt, M. W. I.: Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions, Biogeosciences, 3, 397–420, doi:10.5194/bg-3-397-2006, 2006.
Ritchie, J. C. and McCarty, G. W.: (137)Cesium and soil carbon in a small agricultural watershed, Soil Till. Res., 69, 45–51, doi:10.1016/s0167-1987(02)00127-7, 2003.

BGD
11, 16799–16824, 2014

Rivas, Y., Matus, F., Rumpel, C., Knicker, H., and Garrido, E.: Black carbon contribution in volcanic soils affected by wildfire or stubble burning, Org. Geochem., 47, 41–50, doi:10.1016/j.orggeochem.2012.03.007, 2012.
Rodionov, A., Amelung, W., Haumaier, L., Urusevskaja, I., and Zech, W.: Black carbon in the Zonal steppe soils of Russia, J. Plant Nutr. Soil Sc., 169, 363–369, doi:10.1002/Jpln.200521813, 2006.
Rumpel, C., Chaplot, V., Planchon, O., Bernadou, J., Valentin, C., and Mariotti, A.: Preferential erosion of black carbon on steep slopes with slash and burn agriculture, Catena, 65, 30–40, doi:10.1016/j.catena.2005.09.005, 2006.
Saiz, G., Goodrick, L., Wurster, C. M., Zimmermann, M., Nelson, P. N., and Bird, M. I.: Charcoal re-combustion efficiency in tropical savannas, Geoderma, 219, 40–45, doi:10.1016/j.geoderma.2013.12.019, 2014.
Santos, V. B., Araujo, A. S. F., Leite, L. F. C., Nunes, L. A. P. L., and Melo, W. J.: Soil microbial biomass and organic matter fractions during transition from conventional to organic farming systems, Geoderma, 170, 227–231, doi:10.1016/J.Geoderma.2011.11.007, 2012.
Santín, C., Doerr, S. H., Shakesby, R. A., Bryant, R., Sheridan, G. J., Lane, P. N. J., Smith, H. G., and Bell, T. L.: Carbon loads, forms and sequestration potential within ash deposits produced by wildfire: new insights from the 2009 "Black Saturday" fires, Australia, European J. Forest Res.-Jpn., 131, 1245–1253, doi:10.1007/s10342-012-0595-8, 2012.
Schmidt, M. W. I., Skjemstad, J. O., and Jager, C.: Carbon isotope geochemistry and nanomorphology of soil black carbon: black chernozemic soils in central Europe originate from ancient biomass burning, Global Biogeochem. Cy., 16, 1123, doi:10.1029/2002GB001939, 2002.
Schmidt, M. W. I., Torn, M. S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I. A., Kleber, M., Kogel-Knabner, I., Lehmann, J., Manning, D. A. C., Nannipieri, P., Rasse, D. P., Weiner, S., and Trumbore, S. E.: Persistence of soil organic matter as an ecosystem property, Nature, 478, 49–56, doi:10.1038/nature10386, 2011.
Schneider, M. P. W., Hilf, M., Vogt, U. F., and Schmidt, M. W. I.: The benzene polycarboxylic acid (BPCA) pattern of wood pyrolyzed between 200 degrees C and 1000 degrees C, Org. Geochem., 41, 1082–1088, doi:10.1016/j.orggeochem.2010.07.001, 2010.
Schneider, M. P. W., Pyle, L. A., Clark, K. L., Hockaday, W. C., Masiello, C. A., and Schmidt, M. W. I.: Toward a "Molecular Thermometer" to estimate the charring temperature of wild land charcoals derived from different biomass sources, Environ. Sci. Technol., 47, 11490–11495, doi:10.1021/es401430f, 2013.

BGD
11, 16799–16824, 2014

Singh, N., Abiven, S., Torn, M. S., and Schmidt, M. W. I.: Fire-derived organic carbon in soil turns over on a centennial scale, Biogeosciences, 9, 2847–2857, doi:10.5194/bg-9-2847-2012, 2012.
Slater, C. S. and Carleton, E. A.: The effect of soil erosion on losses of soil organic matter, Soil Sci. Soc. Am. Pro., 3, 123–128, 1938.
Throop, H. L., Archer, S. R., Monger, H. C., and Waltman, S.: When bulk density methods matter: implications for estimating soil organic carbon pools in rocky soils, J. Arid Environ., 77, 66–71, doi:10.1016/J.Jaridenv.2011.08.020, 2012.
Veblen, T. T. and Donnegan, J. A.: Historical Range of Variability for Forest Vegetation of the National Forests of the Colorado Front Range, USDA Forest Service, Golden, CO, 2005.
von Lutzow, M., Kogel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., and Flessa, H.: Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions – a review, Eur. J. Soil Sci., 57, 426–445, 2006.
Wiedemeier, D. B., Hilf, M. D., Smittenberg, R. H., Haberle, S. G., and Schmidt, M. W.: Improved assessment of pyrogenic carbon quantity and quality in environmental samples by high-performance liquid chromatography, J. Chromatogr. A, 1304, 246–250, doi:10.1016/j.chroma.2013.06.012, 2013.
Wohl, E.: Migration of channel heads following wildfire in the Colorado Front Range, USA, Earth Surf. Proc. Land., 38, 1049–1053, doi:10.1002/esp.3429, 2013.
Wood, P. J. and Armitage, P. D.: Biological effects of fine sediment in the lotic environment, Environ. Manage., 21, 203–217, doi:10.1007/s002679900019, 1997.
Ziolkowski, L. A., Chamberlin, A. R., Greaves, J., and Druffel, E. R. M.: Quantification of black carbon in marine systems using the benzene polycarboxylic acid method: a mechanistic and yield study, Limnol. Oceanogr.-Meth., 9, 140–140, doi:10.4319/lom.2011.9.140, 2011.

BGD
11, 16799–16824, 2014

Table 1. Site characteristics (%C, %N, C : N, C stock) of litter, 0–5 cm soils and 5–15 cm soil classified by burn intensity and slope. Mean values reported with standard errors in parentheses.

layer	burn intensity	slope (degrees)	%C	%N	C : N	C stock ($t\,C\,ha^{-1}$)
litter	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)

BGD
11, 16799–16824, 2014

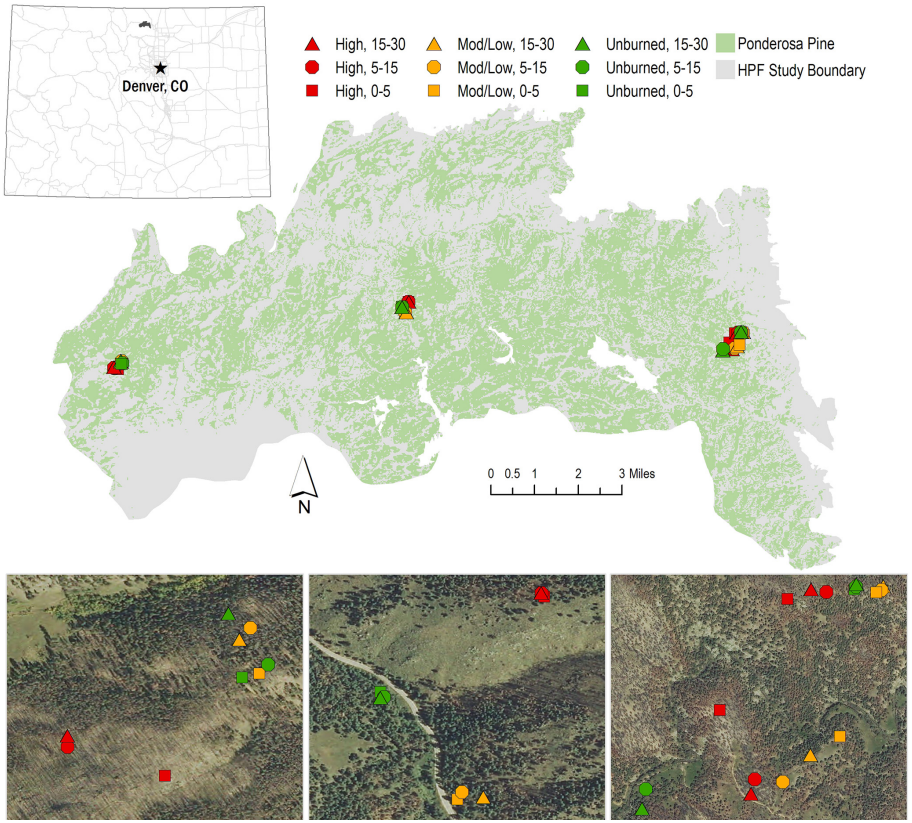

Figure 1. Location and classification (burn intensity, and slope) of study sites within the High Park Fire burn area.

BGD
11, 16799–16824, 2014

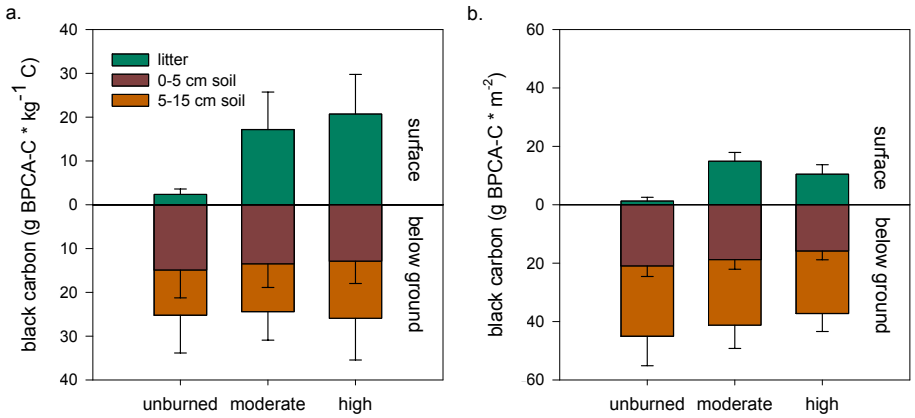

Figure 2. Distribution of black carbon in Ponderosa litter in **(a)** g kg^{-1} C, and **(b)** g m^{-2} in surface (0–5 cm) and subsurface (5–15 cm) soils illustrating the significant difference in unburned vs. moderate and highly burned litter ($p < 0.001$).

BGD
11, 16799–16824, 2014

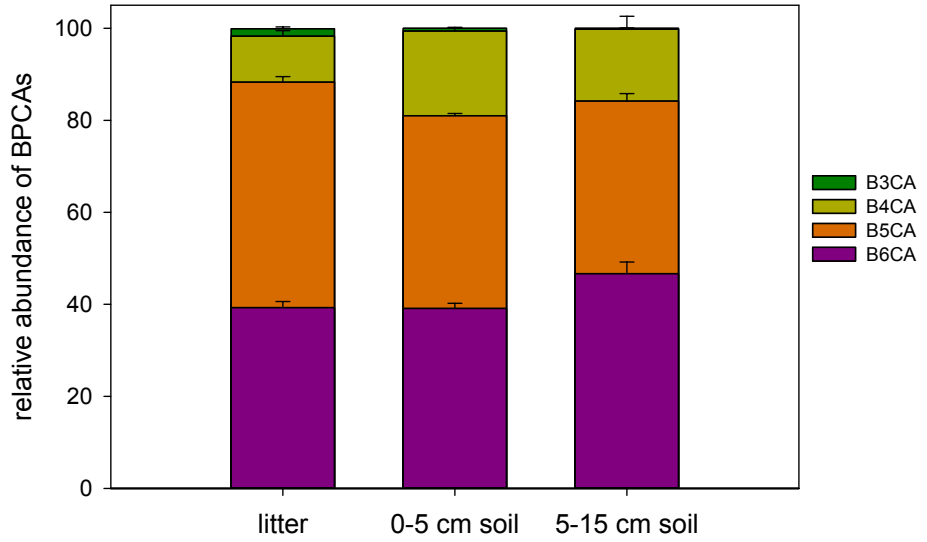

Figure 3. Distribution of BPCAs in each layer illustrating the greatest quantity of B5CA and B3CA in litter ($p < 0.001$), the greatest quantity of B4CA in 0–5 cm soil ($p < 0.001$), and the greatest quantity of B6CA in 5–15 cm soil ($p < 0.001$).

BGD
11, 16799–16824, 2014

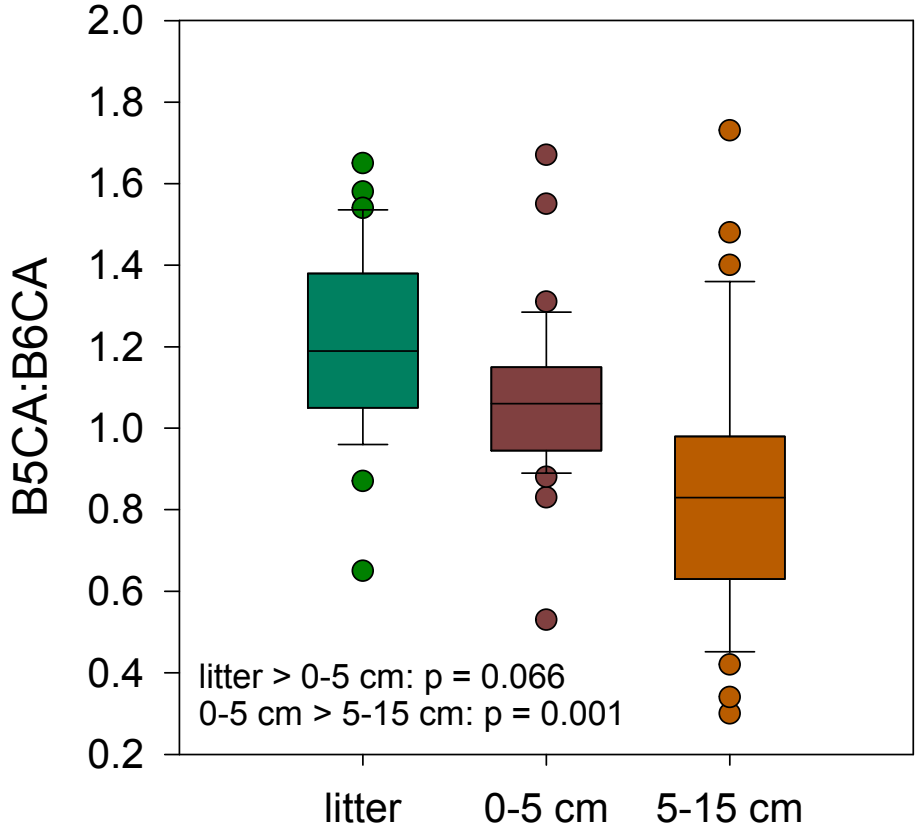

Figure 4. Ratio of B5CA to B6CA illustrating an increasing amount of B6CA and decreasing amount of B5CA with increasing soil depth.

BGD
11, 16799–16824, 2014