Response to comments by D. Wiedemeier:

We have a few technical comments: (1) the usage of a B5CA/B6CA ratio and interpretations about condensation could be better introduced and explained. For example, in the abstract, B5CA/B6CA is described as "less condensed to more condensed BC", which is not fully correct because it actually is just a ratio of less carboxylated to more carboxylated building blocks of a part of BC (B3CA, B4CA exist, too) after BC digestion.

Dr. Weidemeier has very recently published some interesting work where he examining the degree of BC condensation as a ratio of B6CA to total BPCAs. We have revised the abstract and discussion to use the B6CA:total BC to determine the effect of burn intensity and layer on the degree of condensation of BC in light of Dr. Weidemeier's findings. We also describe and maintain the use of B5CA:B6CA as an indication of heat of BC formation as described in Wolf et al. 2013.

The paper that you cited (Rodionov et al. 2006) does not explicitly make this link nor mention BPCA ratios. Moreover, the postulated link in the manuscript between BPCA ratios and degree of processing is still a topic of research and the link between the ratios and age seems rather hypothetical (p 16803).

The reviewer is correct, we provided the wrong citation. It should be Rodionov et al. 2010, Black carbon in grassland ecosystems of the world. Global Biogeochemical Cycles vol. 24 GB3013, doi:10.1029/2009GB003669. We agree the link between age and BPCA ratios has not been well established and have revised the discussion to focus on the potential to relate BPCA ratios with the heat of BC formation.

The fully factorial design of the study allows for a lot of statistics. However, as it is currently presented, it is hard to check if the used statistical methods (ANOVA and post-hoc (F-test?)) really aid data interpretation. Mentioning the number of replicates (also in figures/captions), conducting and showing the residual analysis and model plausibility of ANOVA (in supplement), including a table showing all data including BC (maybe in supplement or extending table 1), and a more trans- parent handling of statistics could enhance the credibility of the findings. For example, F-values do not add much information when p-values are shown and it is pretty risky to state that burn intensity and layer affect %C when their interaction is significant (p. 16807& table S1).

The statistical analyses were repeated using SAS instead of sigmaplot for increased flexibility and better visualization of residual analysis. The Data Analysis section (2.5) was updated to reflect this change. The number of replicates was added to all figure captions and stated more explicitly in the data analysis section. The results of residual analyses are not typically presented in supplemental information for Biogeosciences Discussion papers, so, similar to the full dataset, we have elected to make them available upon request. F-values were removed from data presentation and text in the results section was updated to note the independent effects of burn severity and layer could not be assessed due to the significant interaction term.

Generally, we think that the manuscript could considerably profit from focusing on the main story (post-fire BC distribution) while additional information can be given in the supplement and/or omitted. Shortening would be particularly useful in the Materials and Method section as it is very long, very descriptive and mostly published elsewhere in detail (e.g. density measurement, elemental, BPCA and statistical analysis). Moreover, the "BPCA method validation" has been published before (in our method paper and supplement), yielding the same CV's and linearities on a variety of materials and can therefore be omitted or put into the supplement as a "BPCA setup check".

The manuscript has been refocused to highlight the major findings on post-fire BC distribution, and the methods section was shortened for the BPCA method validation and bulk density determination, the BPCA method validation was moved to the Supplemental Information.

In contrast, some sections could potentially be slightly expanded, for example: Based on the entire BPCA distribution patterns (figure 3), could you distinguish litter BC from soil BC and what are the implications? Or why did you prefer slope as a factor instead of landform (0◦ can be on a peak or in a valley but with very different erosion characteristics)?

The BPCA distribution patterns discussion was expanded, although, as noted in the results, we could distinguish the soil layers (litter vs. 5-15 cm soils, and 0-5 cm soils vs. 5-15 cm soils) based on the proportion of B6CA and B5CA:B6CA. This sentence was added to explain our choice of soil slope versus landform, "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 Ponderosa pine vegetation on difficult to access terrain." (inserted in section 2.2 Litter and soil collection). We also added this statement in the discussion, "The position of our sites on 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 others 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)."

Response to comments by Anonymous Referee #1

Some detail on already published methods section could be reduced, and I would recommend to refocus and polish the Discussion section: - "... BC incorporation processes at depth via water flow and biotic infiltration processes". I was not sure which " biotic infiltration processes" you consider.

The methods section was reduced and the discussion section was expanded and polished. The clause, "stimulated by soil fauna" was added to clarify "biotic infiltration processes" on pg. 16813.

The attempt to relate the ratio B5AC to B6CA to "age" is not substantiated, but if you think so you should explain why you think so

This has been removed and reframed in light of the relationship of B5CA:B6CA on heat of formation.

Is the last paragraph of the Discussion section necessary? "The distribution of BC on a landscape .....transport into the soils bias dissolution and translocation". It did not become clear to me how these conclusions relate to your actual results. Or are these (admittedly reasonable) speculations, but still speculations.

The last paragraph of the discussion should be been included under the conclusions heading. It provides context for the implications of the study. We studied the distribution of BC on the landscape post-fire, and describe how improving our understanding of distribution is meaningful in relationship to how BC functions in soil. Text was added to justify erosion as a dominant loss mechanism (beginning page 16813 following the discussion of rates of incorporation).

Then some more minor remarks: P 16800 L1: communicate clearly and avoid ambigu- ous wording, such as “heterogeneous product of burned biomass”, “critical component of black carbon cycle” L 10: replace “developed and implemented the BPCA method” simply with “used the BPCA method”. I could not see "development" of the BPCA method. It basically reproduces an existing and published method (Wiedemeier et al, 2013). building on previous work (Rodionov et al, 2006, Brodowski et al., Glaser et al.). Adapt wording throughout the text. L15: Explain why you think that none of the post-fire BC has been incorporated to the soil L16: Please explain why you choose to use the ratio B5CA:B6CA, and why you think it can be linked to condensation, age and processing. L25: “is arguably the least understood component of terrestrial C cy- cle” is spurious, there are many other components (microbial etc.), which we do not understand too well yet. Rephrase.

Recommended sentences have all been rephrased to improve clarity.

P16801 L14: “BC particles are composed of a refractory aromatic core and a reactive, oxidized patina” – this may not always be true, especially when considering fresh char. Please rephrase. L11-20: include some more recent publications, e.g. Keiluweit et al., 2010, Wiedemeier et al., 2014 L28: surface topography and geomorphology. Specify why you think that there is a difference between the two.

The statement was rephrased to, “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., 2008; Cheng et al., 2006).”, and “geomorphology” was removed.

P16802 L11: the list of methods is not extensive, therefore use “or” instead of “and”.

The suggested change was made.

P16803 L4-6: Probably you mean BC stocks and not BPCA stocks L17: Could you add the WRB names for the soils?

The suggested change was made to BC stocks, and the WRB names for the soils were added in the statement, “Soils in the montane forests are Alfisols from the great group cryoboralfs and Mollisols from the suborder ustolls (Peet, 1981).”

P16804-P16807: Shorten significantly 16808: "BPCA method validation" seems to be a simple quality check.

The section was shortened as suggested.

P16810 L6: BPCA are molecular markers, not biomarkers. L7: . . . higher proportion of more condensed BC

The suggested changes were made.

P16814 L20: The conclusion’s section is extremely short and probably not complete.

Additional text was added to the conclusions section rephrasing the major findings of the manuscript.

Figure 1 Since you investigate the effect of topography, an elevation map would be more appropriate than airborne/satellite pictures.

The satellite pictures aid in showing the distribution of the vegetation so we have left the figure as is. If the editor requires, we can produce an elevation map as well.

Figure 3 Maybe separate litter visually a bit better from the two soil bars in order to guide the reader.

We feel the green color and indication of surface on the graph are adequate for making the litter distinct. None of the other reviewers commented on this, which suggests that the figure is sufficiently clear.

Table S1-S6 Remove the F-values and make sure you show what is mentioned in the caption, e.g. Table S5, B4CA:B6CA is not shown in the table.

F-values have been removed, and captions were updated.

Response to comments by Anonymous Referee #3

(i) It is clear from the data presented that unburnt litter has a lot less pyrogenic carbon than litter from the burnt sites, which means that the pyrogenic carbon from previous fires has gone 'somewhere'. The authors seem to favour erosional loss as the dominant mechanism for the difference, but its not clear to me why this mechanism is favoured over biotic/abiotic degradation/mineralization (possibly followed by leaching), given the 40-100 year fire return interval, which leaves plenty of time for both degradation and erosion. I don't think its possible to pick between these possibilities based on the data presented, so I would recommend expanding the text to elaborate on the possibility that degradation also a plausible mechanism for loss. Over a few years, with resampling of the sites, it may well be possible to demonstrate that erosion is dominant in this environment, but this can't be uniquely concluded to be the dominant mechanism from a single post-fire sampling. This probably also means softening/modifying some of the conclusions in the abstract as well as parts of the discussion.

Text on the potential for biotic and abiotic degradation mechanisms to contribute to BC losses in this system was added (pg 16813, new paragraph for loss mechanisms following discussion of potential rate of incorporation), and reference to preliminary data discussing the contribution of erosion on BC contents in the CLP was added as well as a reference that describes particulate black carbon export from the CLP following the HPF (Wagner et al. 2015). We have also softened the concluded loss mechanism in the abstract and discussion.

(ii) As I understand it, the BPCA technique likely under-estimates to pyrogenic carbon because the technique cannot completely break down large polyaromatic compounds. This is implied on pp16806 line 27 where conversion factors are mentioned but it should be explicitly stated that to stocks are likely under-estimated by a significant amount - its not a problem for the comparisons in this paper, because like is being compared with like, but it is important in terms of comparing this data with other techniques.

Text added to address this comment (page 16811 at the end of the first paragraph of the discussion) and reinforce the idea that BPCAs are markers for BC comparative analyses, but their measurement underestimates 'true' BC stocks.

(iii) The BPCA analyses were calibrated through an analysis of a 'laboratory biochar'. Please provide further information on the characteristics of this char, and the degree to which it might be representative of natural bushfire chars

The laboratory char was combusted pine wood and details on its production have been added to the supplemental information.

(iv) can you add any information on the likely temperatures achieved in the fire at dif- ferent intensities? This bears particularly on the recalcitrance of the pyrogenic carbon produced in the fire at different intensities, and probably on its observability by BPCA analysis. For example, it is possible that there was 'more' total PyC made during the high intensity fire, but less of it measured by BPCA analysis because a higher propor- tion was not liberated for analysis (ie a correction factor closer to 5 than 2.27. This might explain in part the apparent similarity of stocks between the medium and high intensity burn sites in the litter layer.

As for most of wildfires, we unfortunately do not have any data on the temperature of the fire, although the BPCA pattern is related to the highest temperature achieved, suggesting that, given the similar B6CA content and B5CA:B6CA ratio in moderate and highly burned litter, the temperatures of the fires may have been similar. Text to address this comment has been added (p 16814).

(v) it seems important to include information about whether the sites chosen are all sites of erosion rather than colluvial accumulation, the latter potentially being sites enhanced burial of pyrogenic carbon from previous fires?

It is true that the sites we sampled could experience erosion or accumulation, but given that our study was designed to test the effect of slope rather than landscape position we are unable to evaluate the effect of erosion versus accumulation in a balanced, replicated way. We've added text to the discussion of experimental design (p 16804) and discussion on the effects of slope (p. 16812) that addresses this comment.

Smaller things: Page 16801 line 2 – change in which to during which 16803 – 4 – highly is probably not the right word here 16803 – 7 – I think you means BPCA-C? 16803 – 13 – delete first occurence of the 16811 – 25 – how many rain events of what magnitude? 16813 – 10 – this is a place where the erosion argument is made a bit strongly and could be reworded – there are others.

The suggested changes were made.

Comments by Anonymous Referee #4

1) Assumption of this study: The major constraint to compare the BC stocks in the litter/soil of the unburned sites with a fire history and recently burnt site is that we do not have any knowledge of the production rate of BC in these two sites after wildfire. Therefore, there is high uncertainity with respect to loss of BC or incorporation into the soils. The assumptions made in this study and various constraint should be highlighted.

This study focused on processes contributing to the distribution of BC in soils after it was deposited on the forest floor, and does not address the amount of BC produced in the fire. Different amounts could be deposited from different fires depending on the type of fire, and climate post-fire, however in our discussion of incorporation of BC into soils we explicitly state, "This calculation contains a high degree of uncertainty…" (p. 16813), and have added text that the incorporation rates will also depend on characteristics of the fire (p. 16813).

2) Loss of BC: The presence of BPCA-C in the litter of unburned site indicates fire history. The data indicated that recently burnt sites litter have higher BPCA-C as com- pared to the unburned sites leading the authors to conclude that erosion is the dominant loss mechanism. As mentioned by the authors, the return interval of fire in this site is 40-100 years, it is possible the BC was lost not only via erosion but also through leaching, degradation leading to mineralization/decomposition both biotically as well as

abiotically. The authors should discuss in detail why erosion is the most dominant loss mechanism for this ecosystem and if it is specific to this site. Are there any other study that highlight erosion as one of the prevalent process for this specific site?

We have added text that addresses this comment, expanding the discussion of loss mechanisms (pg 16813, new paragraph for loss mechanisms following discussion of potential rate of incorporation), and referenced preliminary data discussing the contribution of erosion on BC contents in the CLP, as well as a reference that describes particulate black carbon export from the CLP following the HPF (Wagner et al. 2015).

3) Burn intensity and BPCAs: Could authors provide any detail regarding the temper- ature range for the wildfire. Does the moderate and high intensity also had differences in the temperature of the wildfire? This is important because the gradient of change in structure between say 300 and 600 degrees is very steep, so a small change in temperature can induce a large change in BC structure and hence differences in the relative proportions of BPCAs in different burn intensity sites.

As we said above, we had no data on the temperature range of this wildfire. There was no difference in the proportion of B6CA or the B5CA:B6CA ratio between the moderate and highly burned sites (see table S5 where layer is the only significant effect). The discussion of temperature and the BPCA patterns has been expanded to include the effects that were observed by layer (p. 16814).

4) BPCA and age of BC: A word of caution when drawing conclusions from the ra- tios of B5CA and B6CA to the age of BC. There are studies that indicate no change (Schneider et al., 2011) or an increase in B6CA (Hammes et al., 2008) after 100 y or decrease in total aryl group indicating decrease in B6CA (Hilscher and Knicker, 2011). BC with very high proportion of B6CA could also come from high temperature freshly burnt charcoal. It is not clear yet if the changes in the relative contribution of various BPCAs could be linked directly to age of BC. Please clarify what does this ratio implies.

The discussion has been modified to remove conclusions about B5CA:B6CA and BC age, and has been refocused on a discussion of temperature of formation.

5) BPCA pattern of fresh BC produced after wildfire: The type of BC produced during the wildfire in this particular study has not been made very clear. Did litter layer in moderately burned sites majorly constituted of charred needles while high burn inten- sity sites also had some wood charcoal or the type of BC produced were similar? This is important as BC produced would be qualitatively different and hence would have a difference in BPCA pattern. Did authors also measured BPCA of the BC produced (only charcoal pieces and not litter in general)? This is important to compare the BC produced and the processing it underwent while getting incorporated into soil layers.

We described the sites, “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.” The types of BC produced were similar in the highly and moderately burned sites. There were standing, and a few charred logs in both the moderate and highly burned sites, but they were not sampled as part of the soil collection effort, the samples that were collected were as described, “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 (0-5cm) 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.”

6) The data in this study indicated that the stocks of BC in unburned sites and highly burned sites are similar, however, they are distributed differently. It is obvious to have higher BC stocks in the litter layer of the high burn intensity sites compared to unburned sites after wildfire. However, what could be the reasons for lower BC stocks in soils of high burn intensity as compared to unburned sites? Discuss.

BC stocks were not significantly lower in the high burn intensity than unburned sites (see Table S4). The paragraph that discusses this (p. 16812) opens with the idea that burned soils can have lower BC stocks due to combustion of relict BC during recent fires, however we did not we did not find this trend in our system.

7) Validation of BPCA method should be addressed in method section rather than in results as the method was not developed in this study but adopted from previous stuides based on BPCA analysis. Moreover, Methods and material section could be shorten with proper referencing of the method used.

The methods section was shortened and the BPCA method validation was moved to the supplemental information.

Minor corrections

BPCA is molecular marker and not biomarker. Please correct it throughout the manuscript.

It has been corrected.

P16800 L10-remove developed and, "We developed and implemented the benzene polycarboxylic acid (BPCA) method"

It has been removed.

P16800 L12: abbreviate black carbon
P16800 L25: add " one of the least"
P16801 L3: "BC" instead of Black C
P16803 L7: it should be either BC or BPCA-C and not BPC-A

Suggested changes have been made.

P16803 L9-10: rephrase the sentence "We also expected that the BC age and de- gree of processing would increase with depth" . The manuscript does not highlight how BC age was calculated. Instead of degree of processing it should be degree of condensation.

We have made this change.

P16803 L24: HPF was abbreviated here. It should be stated when first used, for eg. in the abstract (P16800 L 4). Be consistent while using abbreviated terms once defined.

We have made this change.

P16813 L9-11: The authors calculated based on this study that 17% of the HPF fire- derived BC in litter would be transferred to the 0–15 cm soil and concluded that the bulk of the BC in this system likely moves off the landscape through surface runoff. How was this conclusion drawn is unclear. Again, the

loss of BC could occur via several other mechanisms including runoffs. This conclusion should be stated as one of the possibilities rather than a clear mechanism occurring in this specific site.

We have added text that addresses this comment, expanding the discussion of loss mechanisms (pg 16813, new paragraph for loss mechanisms following discussion of potential rate of incorporation), and referenced preliminary data discussing the contribution of erosion on BC contents in the CLP, as well as a reference that describes particulate black carbon export from the CLP following the HPF (Wagner et al. 2015).

P16813 L13: what does biotic infliteration processes refers here? Please clarify.

We have added the phrase, 'stimulated by soil fauna' to clarify the meaning of biotic infiltration.

Conclusion: This section here is rather a highlight and appears incomplete. It should include major findings and its implications. The authors should stress on the distribution pattern of BC in different soil layers after wildfire as the major conclusion rather than the loss mechanisms which remain unclear.

The 'conclusions heading' should have been at the beginning of the previous paragraph, and the paragraph has been re-written as suggested.

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

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

(1) Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO 80523

(2) Department of Soil and Crop Sciences, Colorado State University, Fort Collins, CO 80523

Corresponding Author: Claudia M. Boot, claudia.boot@colostate.edu

Claudia 4/7/2015 6:30 AM
Deleted: litter

Abstract

Biomass burning produces black carbon (BC), effectively transferring a fraction of the biomass C from an actively cycling to a passive C pool, which may get 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 took place 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, 0-5 cm soils, and 5-15 cm soils four 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 in burned sites (19 g BPCA-C kg^{-1} C), while BC stocks were greatest in the 5-15 cm subsurface soils (23 g BPCA-C m^{-2}). 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 cm or 5-15 cm soil layers. The ratio of B6CA:total BPCAs, and 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 than 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 from the system, either through erosion events, degradation or translocation to deeper soils. Future work examining mechanisms for BC losses from the forest soil will be required for understanding the role BC plays in the global carbon cycle.

Claudia 4/2/2015 11:57 PM
Deleted: Black

Francesca Cotrufo 4/5/2015 5:47 PM
Deleted: some burned ...iomass C fr ... [1]

Claudia 4/2/2015 11:57 PM
Deleted: the heterogeneous product of burned biomass, is a critical component in the global carbon cycle

Francesca Cotrufo 4/5/2015 5:52 PM
Deleted: ,...Yy ... [2]

Claudia 4/7/2015 6:16 AM
Deleted: litter... 0-5 cm soils, and 5- ... [3]

Claudia Boot 4/3/2015 4:52 PM
Deleted: black carbon

Francesca Cotrufo 4/5/2015 5:55 PM
Deleted: (g BC kg^{-1} C, and g BC m^{-2})

Claudia 4/3/2015 12:03 AM
Deleted: developed and implemented

Claudia Boot 4/3/2015 4:52 PM
Deleted: black carbon

Claudia 4/7/2015 6:17 AM
Deleted: litter

Francesca Cotrufo 4/5/2015 6:07 PM
Deleted: to

Claudia Boot 3/31/2015 3:12 PM
Deleted: B5CA:

Francesca Cotrufo 4/5/2015 6:09 PM
Deleted: (

Claudia Boot 3/31/2015 3:18 PM
Deleted: less condensed to more condensed

Francesca Cotrufo 4/5/2015 6:09 PM
Deleted: BChigher values indicate a greater ...he degree of aromatic C ... [4]

Claudia Boot 3/31/2015 3:20 PM
Deleted: indicated there was significantly more older, more processed BC at depth

Claudia 4/7/2015 6:17 AM
Deleted: litter...and 0-5 cm soils. To ... [5]

Claudia Boot 4/4/2015 5:57 PM
Deleted: leaching

Francesca Cotrufo 4/5/2015 6:14 PM
Deleted: transport

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 × 10^6 ha of boreal and temperate forest and more than 500 × 10^6 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). 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 (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., 2008; Cheng et al., 2006). The degree of condensation of the aromatic core has been shown to be quite variable (McBeath and Smernik, 2009; Wiedemeier et al., 2015d), 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. The shape of a landscape and propensity for erosion versus deposition

Claudia 4/3/2015 12:06 AM
Deleted: arguably

Claudia Boot 4/8/2015 9:54 AM
Deleted: *

Claudia Boot 4/8/2015 9:54 AM
Deleted: *

Claudia 4/3/2015 1:44 AM
Deleted: in

Claudia 4/3/2015 12:20 AM
Deleted: and geomorphology

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 relationship between geomorphology and soil erosion/sediment transport is fairly well understood (Ritchie and McCarty, 2003; Slater and Carleton, 1938), the relationship between soil erosion and fate of different components of SOM that are eroded, including BC, are 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 spectroscopy (NMR) or the quantification of BC-specific molecular markers (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 additional information about BC quality related to its degree of aromatic condensation and aromaticity (Schneider et al., 2010; Schneider et al., 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 June 9th-24th, 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*) (Figure 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

Claudia 4/3/2015 12:22 AM
Deleted: and

Claudia Boot 4/3/2015 4:50 PM
Deleted: bio

Claudia 4/3/2015 12:21 AM
Deleted: , derived from fire temperature and age

Claudia Boot 4/4/2015 6:00 PM
Deleted: ,

Claudia 4/7/2015 6:18 AM
Deleted: litter

Claudia Boot 4/3/2015 4:55 PM
Deleted: High Park fire

Claudia Boot 4/4/2015 5:43 PM
Deleted: intensity

Claudia Boot 4/8/2015 10:01 AM
Deleted: /

understand the degree of condensation of BC through the soil profile. We expected that BC stocks would be the greatest in high burn severity sites, followed by moderate, 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 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 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 lightening strike ignition (Veblen and Donnegan, 2005). A lightening strike started the HPF on June 9, 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 degrees), 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 Ponderosa pine vegetation on difficult to access terrain. Geographic Information System (GIS) layers of land ownership, slope, fire intensity,

Claudia Boot 4/8/2015 10:01 AM
Deleted: age and degree of processing

Claudia 4/3/2015 12:23 AM
Deleted: PCA

Claudia 4/3/2015 1:45 AM
Deleted: hly burned

Claudia Boot 4/4/2015 6:00 PM
Deleted: slope of the hill side

Claudia 4/3/2015 12:24 AM
Deleted: BPCA

Francesca Cotrufo 4/5/2015 6:24 PM
Deleted: BPCA

Claudia Boot 4/4/2015 6:01 PM
Deleted: ,

Claudia Boot 4/4/2015 6:01 PM
Deleted: , and N

Claudia 4/7/2015 6:18 AM
Deleted: litter

Claudia Boot 4/4/2015 6:01 PM
Deleted: and N

Claudia 4/3/2015 1:45 AM
Deleted: highly burned

Claudia 4/3/2015 1:46 AM
Deleted: BC age and degree of processing

Claudia 4/3/2015 1:46 AM
Deleted: increase

Claudia 4/2/2015 11:41 PM
Deleted: *d*

Claudia Boot 4/8/2015 10:02 AM
Deleted: p

Claudia Boot 4/8/2015 10:03 AM
Deleted: -

Claudia Boot 4/8/2015 10:03 AM
Deleted: J

Claudia Boot 4/4/2015 5:43 PM
Deleted: intensity

Claudia Boot 4/4/2015 6:04 PM
Deleted: due to the logistical constraints of locating representative areas that met all the desired

Claudia Boot 4/4/2015 6:04 PM
Deleted: on

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 (Figure 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.

insert Figure 1

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 cm and 5-15 cm depth. Due to the high surface variability, 4 additional forest floor samples and 3 surface (0-5cm) soil samples were collected at each site, positioning the frame orthogonally to 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 Supplemental Information). 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 hours for dry weight correction. Forest floor samples were

Claudia Boot 4/4/2015 5:43 PM
Deleted: intensity

Claudia 4/7/2015 6:38 AM
Deleted: and

Claudia 4/7/2015 6:21 AM
Deleted: *Litter*

Claudia 4/7/2015 6:21 AM
Deleted: litter

Claudia 4/7/2015 6:22 AM
Deleted: litter

Francesca Cotrufo 4/5/2015 6:26 PM
Deleted: *

Claudia 4/7/2015 6:22 AM
Deleted: litter

Claudia Boot 4/8/2015 10:05 AM
Deleted: and

Claudia Boot 4/8/2015 10:05 AM
Deleted: the help of

Claudia 4/7/2015 6:22 AM
Deleted: litter

Claudia 4/7/2015 6:22 AM
Deleted: litter

Claudia 4/2/2015 11:17 PM
Deleted: 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 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.

Claudia 4/7/2015 6:22 AM
Deleted: plant

Claudia 4/7/2015 6:23 AM
Deleted: *Litte*

Claudia Boot 4/8/2015 10:06 AM
Deleted: *and*

Claudia 4/7/2015 6:23 AM
Deleted: litter

Claudia 4/7/2015 6:23 AM
Deleted: Litter

then air-dried and another subsample taken and heated in a muffle furnace at 600°C for 12 hours 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 hours 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 (BPCA) as described by (Wiedemeier et al., 2013). The BPCA method was validated with biochar amended soils from the field site (see Supplemental Information). Briefly, 50-150 mg of finely ground, oven dried sample was digested with 70% nitric acid for 8 hours 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 um particle

Claudia 4/7/2015 6:23 AM
Deleted: litter

Claudia 4/7/2015 6:26 AM
Deleted: litter

Francesca Cotrufo 4/5/2015 6:31 PM
Deleted:

Claudia Boot 4/3/2015 4:44 PM
Deleted: The soil was then 8mm 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 2mm sieving, a subsample was taken, finely ground and dried overnight at 105°C.

Claudia Boot 4/8/2015 10:08 AM
Deleted: s

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia 4/7/2015 6:28 AM
Deleted: litter

Claudia 4/2/2015 11:13 PM
Deleted: For the BPCA analysis,

size, 2.1 x 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/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). 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 cm soil, 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^{-2}) to meet assumptions of equal variance and normality, which were assessed with Studentized residual diagnostic plots. The null hypothesis, that the independent factor had no effect, or that no linear correlation existed between variables, for all tests was evaluated at $\alpha < 0.05$. Analyses were run using SAS 9.4.

3. Results

3.1 Percent and Stocks of C and N in Forest floor and Soil

Values for %C ranged from 29% in the forest floor to 0.9% C in the 5-15 cm soil layer, for %N from 0.8% in forest floor to 0.08% in the 5-15 cm soil layer, and for C:N from 40 in

Claudia 4/2/2015 11:15 PM
Deleted: a gradient method consisting of mobile phase A: HPLC grade water with 25 mL/L 85% orthophosphoric acid buffered with monosodium phosphate to pH 1.2, and mobile phase B: acetonitrile. Gradient separation was 0-5 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-equilibratio... [6]

Claudia Boot 4/8/2015 10:11 AM
Deleted: (... ADDIN EN.CITE (Brodo... [7]

Claudia 4/2/2015 10:32 PM
Deleted: 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. ...he effects ... [8]

Claudia Boot 4/4/2015 6:07 PM
Deleted: and

Claudia 4/2/2015 10:03 PM
Deleted: as...compared using three-... [9]

Claudia Boot 4/4/2015 6:08 PM
Deleted: Linear regression for BPCA method validation was evaluated using Pearson's *R*.

Claudia 4/2/2015 10:05 PM
Deleted: . ANOVA and regression analyses

Claudia Boot 4/8/2015 10:12 AM
Deleted: SAS x.xxSigmaPlot 12.5 (Systat Software, San Jose, CA).

Claudia 4/2/2015 10:05 PM
Formatted: Highlight

Claudia 4/7/2015 6:28 AM
Deleted: *Litter*

Claudia 4/7/2015 6:28 AM
Deleted: litter...orest floor to 0.9%... [10]

798 the forest floor to 13 in 5-15 cm soil. We tested for effects of layer, burn severity, slope and
799 their interactions and found that the main effects were distinct for each response variable
800 (%C, %N and C:N). Effects of burn severity (p=0.002) and layer (<0.001) on %C, could not
801 be independently assessed because the burn × layer interaction was also significant
802 (p<0.001, Table S1). Only layer had an effect on %N (p<0.001), while the C:N ratio was
803 affected by slope (p=0.009), burn intensity (p<0.001), layer (p<0.001) and in interaction
804 (p<0.001).

805 **insert Table 1**

806 Post hoc comparisons (Table S2) confirmed expected decreases in %C and %N from
807 forest floor to 5-15 cm soil (p<0.001 for each successive layer), along with a decreasing C:N
808 from forest floor to 0-5 cm soil (p<0.001) and with no change between 0-5 cm and 5-15 cm
809 soil (p=0.703). The burn severity × layer interaction term illustrated that the effects of burn
810 were confined to the forest floor layer for %C and C:N. Within the forest floor layer,
811 unburned sites had greater %C than moderately burned (p=0.009) or highly burned sites
812 (p<0.001), and moderately burned sites also had greater %C than highly burned sites
813 (p<0.001). For the C:N ratio the pattern was the same: C:N was widest in unburned sites
814 which decreased significantly at moderately burned sites (p<0.001) and further still at
815 highly burned sites (p<0.001). Interestingly, slope also had an effect on the C:N. Post hoc
816 comparisons indicated that C:N on 0-5 slopes was lower than 5-15 degree slopes (p=0.028)
817 and the C:N on 0-5 degree slopes was significantly lower than 15-30 degree slopes
818 (p=0.012), while the 5-15 and 15-30 degree slopes were not different (p=0.916).

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

824

825 *3.2. Benzene Polycarboxylic Acid-C in forest floor and soil*

826 We determined BPCA-C both in reference to the amount of carbon and the stock by
827 volume of soil or forest floor and found highly variable amounts of BPCA-C for both
828 metrics. For forest floor, concentration values ranged from 0.09 g kg^{-1} OC in unburned

Claudia 4/7/2015 6:28 AM
Deleted: litter...orest floor to 13 in ... [11]

Claudia Boot 4/4/2015 5:44 PM
Deleted: intensity

Claudia 4/2/2015 10:52 PM
Deleted: affected

Claudia Boot 4/8/2015 10:13 AM
Deleted: (p<0.001 for both)... coul ... [12]

Claudia 4/7/2015 6:50 AM
Deleted: re was...a ...urn × layer ... [13]

Francesca Cotrufo 4/5/2015 6:42 PM
Deleted: the burn × layer

Claudia 4/7/2015 6:53 AM
Deleted: for each)

Claudia 4/7/2015 6:29 AM
Deleted: litter...orest floor to 5-15 ... [14]

Claudia Boot 4/4/2015 5:44 PM
Deleted: intensity ...everity × by ... [15]

Claudia 4/7/2015 6:29 AM
Deleted: litter...orest floor layer fo ... [16]

Claudia Boot 4/8/2015 10:15 AM
Deleted: =0.029

Claudia 4/2/2015 10:58 PM
Deleted: =0.001.... For the C:N rati ... [17]

Claudia 4/7/2015 6:29 AM
Deleted: litter

Claudia Boot 4/8/2015 10:16 AM
Deleted: Using a three-way ANOVA mixed model to evaluate effects of layer, burn intensity severity,and slope and all interactions, the

Claudia 4/7/2015 6:29 AM
Deleted: litter...orest floor having ... [18]

Claudia 4/2/2015 11:12 PM
Deleted:
3.

Claudia 4/2/2015 11:12 PM
Deleted: ....23... *Benzene Polycarbo* ... [19]

Claudia Boot 4/4/2015 5:54 PM
Deleted: The BPCA method was validated with biochar amended soils (see Supplemental Information).

Claudia 4/7/2015 6:29 AM
Deleted: litter...orest floor and fou ... [20]

forest floor, to 40.0 g kg^{-1} OC in highly burned forest floor, and for stocks from 0.1 g m^{-2} in unburned forest floor to 19.52 g m^{-2} in moderately burned forest floor. 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 severity and layer were the main effects on the concentration and stock of BPCA-C (Figure 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 degrees: 18.2 +/- 7.1 g m^{-2}; 5-15 degrees: 14.8 +/- 4.7 g m^{-2}, 15-30 degrees: 11.8 +/- 4.3 g m^{-2}), 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, 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 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, 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 0-5 and 5-15 cm soils (p=0.023, p=0.027, respectively), whereas the stock of BPCA-C was not significantly different in the high burn among forest floor and soil layers.

insert Figure 2

We expected that the layer (forest floor, 0-5 cm soil, 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

Claudia 4/7/2015 6:29 AM
Deleted: litter...orest floor, to 40.0 ... [21]

Claudia Boot 4/4/2015 5:45 PM
Deleted: intensity

Claudia 4/2/2015 10:47 PM
Deleted: three way ANOVA...(slope ... [22]

Claudia Boot 4/8/2015 10:33 AM
Deleted: x

Claudia 4/2/2015 11:04 PM
Deleted: 223

Claudia Boot 4/8/2015 10:33 AM
Deleted: x

Claudia 4/2/2015 11:04 PM
Deleted: 724...40) on BC concentra ... [23]

Claudia Boot 4/4/2015 5:45 PM
Deleted: intensity

Claudia 4/2/2015 11:05 PM
Deleted: 541

Claudia Boot 4/4/2015 5:45 PM
Deleted: intensity ...everity and lay ... [24]

Claudia 4/7/2015 6:29 AM
Deleted: litter

Claudia Boot 4/4/2015 5:45 PM
Deleted: intensity

Claudia 4/7/2015 6:29 AM
Deleted: litter

Claudia Boot 4/8/2015 10:35 AM
Deleted: 3... respectively) and stoc ... [25]

Claudia 4/7/2015 6:29 AM
Deleted: litter

Claudia Boot 4/8/2015 10:36 AM
Deleted: 0

Claudia 4/7/2015 6:29 AM
Deleted: litter

Claudia Boot 4/8/2015 10:36 AM
Deleted: 8... p=0.0272 ... [26]

Claudia 4/7/2015 6:29 AM
Deleted: litter...orest floor and soil ... [27]

Claudia 4/7/2015 6:29 AM
Deleted: litter

Claudia Boot 4/4/2015 5:46 PM
Deleted: intensity

Claudia 4/3/2015 12:31 AM
Deleted: biomarkers...(Rodionov ... [28]

Claudia Boot 4/8/2015 10:37 AM
Deleted: , more processed BC indicated

Claudia 4/2/2015 11:07 PM
Deleted: B5CA,

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 then 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, Figure 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 forest floor layers ($p<0.001$); B5CA was greater in the forest floor 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 ($p=0.037$); B4CA was greater in 0-5 cm soil than in forest floor ($p<0.001$), and 5-15 cm soil ($p=0.002$), with no difference in forest floor and 5-15 cm soil ($p=0.148$). 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 significantly greater in the forest floor than 5-15 cm soils ($p=0.001$) (Figure 3, Table S6)).

insert Figure 3

4. Discussion

Our primary objective was to determine the C socks, 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) 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 organic C and 0-80 g/m^2 (Czimczik et al., 2003; Czimczik et al., 2005; Rodionov et al., 2006). Excluding unburned forest floor samples, we found values within this range, averaging 14 (± 7) g BPCA-C kg^{-1} C, and 19 (± 5) g BPCA-C per m^2. It is important to note that BPCAs are markers for BC, and their total amount is two to five times lower

Claudia Boot 4/8/2015 10:38 AM
Deleted: more than...pproximately ... [29]

Claudia 4/7/2015 6:29 AM
Deleted: litter...orest floor layers ... [30]

Claudia Boot 4/8/2015 10:42 AM
Deleted: 1.... The ratio of B5CA:B6(... [31]

Claudia 4/7/2015 6:29 AM
Deleted: litter

Claudia Boot 4/3/2015 4:12 PM
Deleted: and 0-5 cm s...han 5-15 cr ... [32]

Claudia Boot 4/4/2015 6:09 PM
Formatted: Centered

Claudia Boot 4/4/2015 6:09 PM
Formatted: Font:Bold

Claudia Boot 3/31/2015 3:36 PM
Deleted: **insert Figures 3**

Claudia Boot 3/31/2015 3:36 PM
Formatted: Left, Indent: First line: 0"

Claudia Boot 4/8/2015 11:21 AM
Deleted: and

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia Boot 4/3/2015 4:55 PM
Deleted: High Park fire

Claudia 4/7/2015 6:30 AM
Deleted: litter...orest floor samples ... [33]

Claudia Boot 4/6/2015 9:47 AM
Deleted: a

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^{-1} of C, suggesting a persistent BC pool from past fires. Within the forest floor 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 after the HPF persisted in the forest floor 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 forest floor layer in both highly and moderately burned areas on a per unit 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 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 on 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 others at valley bottoms. In addition, the landscape position

Claudia 4/7/2015 6:55 AM
Deleted: method underestimates

Claudia 4/7/2015 6:55 AM
Deleted: , which may beby two to five times the measured BPCA-C amounts, and

Claudia Boot 4/4/2015 5:46 PM
Deleted: intensity

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia Boot 4/4/2015 5:46 PM
Deleted: intensity

Claudia Boot 4/8/2015 11:25 AM
Deleted: s

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia 4/3/2015 1:30 AM
Deleted: also

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 (~14 g BPCA-C kg^{-1}), while on a per m^2 basis, moderately burned material had greater BC content (20 g BPCA-C m^{-2}) than unburned material (17 g BPCA-C m^{-2}). 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 in 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 (Figure 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 forest floor from the HPF. These data suggest

Claudia 4/2/2015 11:35 PM
Deleted: .

Claudia Boot 3/31/2015 3:37 PM
Deleted: must

Claudia Boot 3/31/2015 3:37 PM
Deleted: be

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia Boot 4/8/2015 11:28 AM
Deleted: oes

Claudia Boot 4/4/2015 3:37 PM
Deleted: (Czimczik et al., 2003)

Claudia Boot 4/4/2015 5:30 PM
Deleted: In

Claudia Boot 4/4/2015 5:30 PM
Deleted: identical

Claudia Boot 4/4/2015 3:46 PM
Formatted: Superscript

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia 4/7/2015 6:30 AM
Deleted: litter

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 forest floor (~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 for BC would result in decreased incorporation, and the reverse for a shorter residence time, and 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 characteristic value for 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 in burned sites if incorporation to deep soil was the dominant mechanism. An additional alternative is 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 three 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 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 Cache la Poudre (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.

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia Boot 4/4/2015 4:46 PM
Deleted: These values...he estimat... [34]

Claudia 4/7/2015 7:30 AM
Deleted: microbial...degradation, ... [35]

Francesca Cotrufo 4/5/2015 6:54 PM
Deleted: also

Claudia 4/7/2015 7:30 AM
Deleted: NEED LINE AND REF FOR ABIOTIC DEGRADATION, CHECK ZIMMERMAN CHAPTER.

Claudia Boot 4/6/2015 10:14 AM
Formatted: Highlight

Claudia Boot 4/3/2015 1:57 PM
Deleted: through surface runoff. ... [36]

Claudia 4/2/2015 11:43 PM
Deleted:

Claudia Boot 4/4/2015 4:48 PM
Deleted: 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 in burned sites if incorporation to deep soil was the dominant mechanism. An additional alternative is loss of BC through microbial degradation as a proportion of BC is known to be labile (Zimmerman, 2010)

Claudia 4/3/2015 12:51 AM
Deleted: Each

Claudia Boot 4/4/2015 4:56 PM
Deleted: for loss

Claudia 4/3/2015 12:38 AM
Deleted: transport could

Claudia Boot 4/4/2015 6:14 PM
Deleted: watershed

Claudia 4/3/2015 12:51 AM
Deleted: and will be largely dependent on

Claudia Boot 4/4/2015 5:18 PM
Deleted: along with climatic variation and the molecular characteristics of BC following wildfires... preliminary BC... [37]

Claudia Boot 4/4/2015 5:03 PM
Moved (insertion) [1]

Claudia Boot 4/4/2015 6:14 PM
Deleted: . ... and...long with a repor... [38]

Claudia Boot 4/4/2015 5:03 PM
Moved up [1]: (Boot et al., 2014).

Our third objective was to describe the distribution of BPCAs within forest floor and soil layers to determine if the molecular structure of BC was characteristic by layer or influenced by burn severity. Recently, Wiedemeir and others validated that the proportion of B6CAs relative to the total BPCAs measured directly correlated with both the degree of condensation and aromaticity of chars, thus we used the relative abundance of B6CA:total BPCA to describe the molecular features of BC (Figure 3). We found that B6CA relative abundance was greater in the 5-15 cm soils relative to forest floor, suggesting that greater more condensed BC, is present in deeper soils at these sites, and 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).

Forest fire temperatures are difficult to determine and can range from approximately 1000 °C in the canopy, a maximum of 850 °C at the surface, averaging approximately 300 °C, 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 of BC deposited on the soil surface following the fire, it must be noted that surface and soil BC is likely a pool integrated across sources pyrolized 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 among B6CA concentrations and temperature of charring for pine needle or leaf derived chars (Schneider et al., 2010; Schneider et al., 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/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, corresponding to 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

Claudia Boot 4/1/2015 1:12 PM
Deleted: ...biomarkers ... [39]

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia Boot 4/1/2015 11:05 AM
Deleted: molecular

Claudia 4/2/2015 12:18 PM
Deleted: is

Claudia Boot 4/8/2015 11:31 AM
Deleted: of forest floor or soil ...y l ... [40]

Claudia 4/2/2015 12:21 PM
Deleted: altered with increasing d ... [41]

Claudia Boot 4/1/2015 10:56 AM
Deleted: intensity

Claudia 4/2/2015 12:40 PM
Deleted: 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).

Claudia Boot 4/1/2015 1:31 PM
Deleted:

Claudia 4/2/2015 12:11 PM
Deleted: The relative abundance of B6CA has been associated with the highest heat treatment temperature (HTT) with the proportion of B6CA increasing with increasing HTT (Schneider et al., 2013) and the proportion of B6CA to total BPCAs can be used to estimate both the degree of condensation and aromaticity ... Other studies have suggested that the pattern of BPCAs may be informative for deter ... [42]

Claudia Boot 4/1/2015 1:56 PM
Deleted: The distribution of the BPCA biomarkers with increasing amount ... [43]

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia Boot 4/1/2015 10:57 AM
Deleted: and a decreasing ratio of B5CA:B6CA with...depth ...uggests... ... [44]

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia Boot 4/3/2015 2:53 PM
Deleted: (Schneider et al., 2013)We also observed that the litter had the grea ... [45]

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. Conclusion

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 forest floor four-months post burn regardless of slope, and was formed at an average temperature of 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.

Author Contribution

MFC and KP designed the experiment, MH coordinated and executed field sampling and site characteristic analyses, MH and CMB performed BPCA analyses, CMB prepared the manuscript.

Claudia Boot 4/4/2015 4:00 PM
Deleted:

Claudia 4/2/2015 12:39 PM
Deleted: This could

Claudia 4/2/2015 12:40 PM
Deleted: a

Claudia 4/2/2015 12:40 PM
Deleted: for BC in the deeper soil la

Claudia Boot 4/3/2015 2:50 PM
Deleted: (Abiven et al., 2011)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 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). .

Claudia Boot 4/6/2015 10:14 AM
Formatted: Indent: First line: 0"

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia Boot 4/8/2015 11:36 AM
Deleted: layer

Claudia Boot 4/4/2015 5:37 PM
Deleted: ,

Claudia Boot 4/4/2015 5:39 PM
Deleted: and that its s

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia Boot 4/3/2015 4:37 PM
Deleted: and

Claudia 4/3/2015 12:50 AM
Deleted: developed the BPCA method,

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. 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).

Claudia 4/2/2015 11:24 PM
Deleted: and

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 Biology & Biochemistry, 43, 1615-1617, 2011.

Baldock, J. A. and Smernik, R. J.: Chemical composition and bioavailability of thermally, altered Pinus resinosa (Red Pine) wood, Organic Geochemistry, 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 Biogeochemical Cycles, 13, 923-932, 1999.

Bird, M. I., Wynn, J. G., Saiz, G., Wurster, C. M., and McBeath, A.: The Pyrogenic Carbon Cycle, Annual Review of Earth and Planetary Sciences, 43, 150223150959000, 2015.

Boot, C. M., Cotrufo, M. F., Haddix, M. L., Schmeer, S., Kampf, S., Brogan, D., Nelson, P., Rhoades, C. C., Ryan-Burkett, S., Rathburn, S., and Hall, E. K.: Transport of Black Carbon Following Wildfire: Contributions of Short and Long-term Controls, American Geophysical Union, San Francisco, CA, 2014.

Brodowski, S., Rodionov, A., Haumaier, L., Glaser, B., and Amelung, W.: Revised black carbon assessment using benzene polycarboxylic acids, Organic Geochemistry, 36, 1299-1310, 2005.

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. Acta, 72, 1598-1610, 2008.

Cheng, C. H., Lehmann, J., Thies, J. E., Burton, S. D., and Engelhard, M. H.: Oxidation of black carbon by biotic and abiotic processes, Organic Geochemistry, 37, 1477-1488, 2006.

Christensen, B. T.: Carbon in primary and secondary organomineral complexes. In: Structure and Organic Matter Storage in Agricultural Soils, Carter, M. R. and Stewart, B. A. (Eds.), CRC Press, Inc, Boca Raton, FL., 1996.

1501 Cusack, D. F., Chadwick, O. A., Hockaday, W. C., and Vitousek, P. M.: Mineralogical controls
1502 on soil black carbon preservation, Global Biogeochemical Cycles, 26, n/a-n/a, 2012.

1503 Czimczik, C. I. and Masiello, C. A.: Controls on black carbon storage in soils, Global
1504 Biogeochemical Cycles, 21, n/a-n/a, 2007.

1505 Czimczik, C. I., Preston, C. M., Schmidt, M. W. I., and Schulze, E.-D.: How surface fire in
1506 Siberian Scots pine forests affects soil organic carbon in the forest floor: Stocks, molecular
1507 structure, and conversion to black carbon (charcoal), Global Biogeochemical Cycles, 17,
1508 n/a-n/a, 2003.

1509 Czimczik, C. I., Schmidt, M. W. I., and Schulze, E. D.: Effects of increasing fire frequency on
1510 black carbon and organic matter in Podzols of Siberian Scots pine forests, European Journal
1511 of Soil Science, 56, 417-428, 2005.

1512 DeBano, L. F.: The role of fire and soil heating on water repellency in wildland enviroments:
1513 a review, Journal of Hydrology, 231-232, 195-206, 2000.

1514 Foereid, B., Lehmann, J., and Major, J.: Modeling black carbon degradation and movement in
1515 soil, Plant and Soil, 345, 223-236, 2011.

1516 Forbes, M. S., Raison, R. J., and Skjemstad, J. O.: Formation, transformation and transport of
1517 black carbon (charcoal) in terrestrial and aquatic ecosystems, The Science of the total
1518 environment, 370, 190-206, 2006.

1519 Glaser, B., Haumaier, L., Guggenberger, G., and Zech, W.: Black carbon in soils: the use of
1520 benzenecarboxylic acids as specific markers, Organic Geochemistry, 29, 811-819, 1998.

1521 Goldammer, J. G. and Crutzen, P. J.: Fire in the Environment: Scientific Rationale and
1522 Summary of Results of the Dahlem Workshop. In: Fire in the Environment: The Ecological,
1523 Atmospheric and Climatic Importance, Crutzen, P. J. and Goldammer, J. G. (Eds.), 1993.

1524 Hammes, K., Schmidt, M. W. I., Smernik, R. J., Currie, L. A., Ball, W. P., Nguyen, T. H.,
1525 Louchouarn, P., Houel, S., Gustafsson, Ö., Elmquist, M., Cornelissen, G., Skjemstad, J. O.,
1526 Masiello, C. A., Song, J., Peng, P. a., Mitra, S., Dunn, J. C., Hatcher, P. G., Hockaday, W. C., Smith,
1527 D. M., Hartkopf-Fröder, C., Böhmer, A., Lüer, B., Huebert, B. J., Amelung, W., Brodowski, S.,
1528 Huang, L., Zhang, W., Gschwend, P. M., Flores-Cervantes, D. X., Largeau, C., Rouzaud, J.-N.,
1529 Rumpel, C., Guggenberger, G., Kaiser, K., Rodionov, A., Gonzalez-Vila, F. J., Gonzalez-Perez, J.
1530 A., de la Rosa, J. M., Manning, D. A. C., López-Capél, E., and Ding, L.: Comparison of
1531 quantification methods to measure fire-derived (black/elemental) carbon in soils and
1532 sediments using reference materials from soil, water, sediment and the atmosphere, Global
1533 Biogeochemical Cycles, 21, n/a-n/a, 2007.

1534 Hammes, K., Torn, M. S., Lapenas, A. G., and Schmidt, M. W. I.: Centennial black carbon
1535 turnover observed in a Russian steppe soil, Biogeosciences, 5, 1339-1350, 2008.

Keiluweit, M., Nico, P. S., Johnson, M. G., and Kleber, M.: Dynamic molecular structure of plant biomass-derived black carbon (biochar), Environmental Science & Technology, 44, 1247-1253, 2010.

Knicker, H.: Pyrogenic organic matter in soil: Its origin and occurrence, its chemistry and survival in soil environments, Quaternary International, 243, 251-263, 2011.

Lehmann, J.: Bio-energy in the black, Frontiers in Ecology and the Environment, 5, 381-387, 2007.

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, Glob. Biogeochem. Cycle, 19, 2005.

Major, J., Lehmann, J., Rondon, M., and Goodale, C.: Fate of soil-applied black carbon: downward migration, leaching and soil respiration, Global Change Biology, 16, 1366-1379, 2010.

Masiello, C. A.: New directions in black carbon organic geochemistry, Marine Chemistry, 92, 201-213, 2004.

McBeath, A. V. and Smernik, R. J.: Variation in the degree of aromatic condensation of chars, Organic Geochemistry, 40, 1161-1168, 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 Science Society of America Journal, 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 Science Society of America Journal, 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, 2006.

Ritchie, J. C. and McCarty, G. W.: (137)Cesium and soil carbon in a small agricultural watershed, Soil & Tillage Research, 69, 45-51, 2003.

Rivas, Y., Matus, F., Rumpel, C., Knicker, H., and Garrido, E.: Black carbon contribution in volcanic soils affected by wildfire or stubble burning, Organic Geochemistry, 47, 41-50, 2012.

1570 Rodionov, A., Amelung, W., Haumaier, L., Urusevskaja, I., and Zech, W.: Black carbon in the
1571 Zonal steppe soils of Russia, Journal of Plant Nutrition and Soil Science, 169, 363-369, 2006.

1572 Rumpel, C., Ba, A., Darboux, F., Chaplot, V., and Planchon, O.: Erosion budget and process
1573 selectivity of black carbon at meter scale, Geoderma, 154, 131-137, 2009.

1574 Rumpel, C., Chaplot, V., Planchon, O., Bernadou, J., Valentin, C., and Mariotti, A.: Preferential
1575 erosion of black carbon on steep slopes with slash and burn agriculture, Catena, 65, 30-40,
1576 2006.

1577 Saiz, G., Goodrick, L., Wurster, C. M., Zimmermann, M., Nelson, P. N., and Bird, M. I.: Charcoal
1578 re-combustion efficiency in tropical savannas, Geoderma, 219, 40-45, 2014.

1579 Santín, C., Doerr, S. H., Shakesby, R. A., Bryant, R., Sheridan, G. J., Lane, P. N. J., Smith, H. G.,
1580 and Bell, T. L.: Carbon loads, forms and sequestration potential within ash deposits
1581 produced by wildfire: new insights from the 2009 'Black Saturday' fires, Australia,
1582 European Journal of Forest Research, 131, 1245-1253, 2012.

1583 Santos, V. B., Araujo, A. S. F., Leite, L. F. C., Nunes, L. A. P. L., and Melo, W. J.: Soil microbial
1584 biomass and organic matter fractions during transition from conventional to organic
1585 farming systems, Geoderma, 170, 227-231, 2012.

1586 Schmidt, M. W. I., Skjemstad, J. O., and Jager, C.: Carbon isotope geochemistry and
1587 nanomorphology of soil black carbon: Black chernozemic soils in central Europe originate
1588 from ancient biomass burning, Global Biogeochemical Cycles, 16, 2002.

1589 Schmidt, M. W. I., Torn, M. S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I. A., Kleber,
1590 M., Kogel-Knabner, I., Lehmann, J., Manning, D. A. C., Nannipieri, P., Rasse, D. P., Weiner, S.,
1591 and Trumbore, S. E.: Persistence of soil organic matter as an ecosystem property, Nature,
1592 478, 49-56, 2011.

1593 Schneider, M. P. W., Hilf, M., Vogt, U. F., and Schmidt, M. W. I.: The benzene polycarboxylic
1594 acid (BPCA) pattern of wood pyrolyzed between 200 degrees C and 1000 degrees C,
1595 Organic Geochemistry, 41, 1082-1088, 2010.

1596 Schneider, M. P. W., Pyle, L. A., Clark, K. L., Hockaday, W. C., Masiello, C. A., and Schmidet, M.
1597 W. I.: Toward a "Molecular Thermometer" to Estimate the Charring Temperature of Wild
1598 land Charcoals Derived from Different Biomass Sources, Environmental Science &
1599 Technology, 47, 11490-11495, 2013.

1600 Singh, N., Abiven, S., Torn, M. S., and Schmidt, M. W. I.: Fire-derived organic carbon in soil
1601 turns over on a centennial scale, Biogeosciences, 9, 2847-2857, 2012.

1602 Slater, C. S. and Carleton, E. A.: The effect of soil erosion on losses of soil organic matter, Soil
1603 Science Society of America Proceedings, 3, 123-128, 1938.

Stewart, C. E., Zheng, J., Botte, J., and Cotrufo, M. F.: Co-generated fast pyrolysis biochar mitigates green-house gas emissions and increases carbon sequestration in temperate soils, GCB Bioenergy, 5, 153-164, 2013.

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, 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.

Wagenbrenner, J. W. and Robichaud, P. R.: Post-fire bedload sediment delivery across spatial scales in the interior western United States, Earth Surface Processes and Landforms, 39, 865-876, 2014.

Wagner, S., Cawley, K. M., Rosario-Ortiz, F. L., and Jaffé, R.: In-stream sources and links between particulate and dissolved black carbon following a wildfire, Biogeochemistry, doi: 10.1007/s10533-015-0088-1, 2015. 2015.

Wiedemeier, D. B., Abiven, S., Hockaday, W. C., Keiluweit, M., Kleber, M., Masiello, C. A., McBeath, A. V., Nico, P. S., Pyle, L. A., Schneider, M. P. W., Smernik, R. J., Wiesenberg, G. L. B., and Schmidt, M. W. I.: Aromaticity and degree of aromatic condensation of char, Organic Geochemistry, 78, 135-143, 2015a.

Wiedemeier, D. B., Brodowski, S., and Wiesenberg, G. L.: Pyrogenic molecular markers: linking PAH with BPCA analysis, Chemosphere, 119, 432-437, 2015d.

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, Journal of chromatography. A, 1304, 246-250, 2013.

Wohl, E.: Migration of channel heads following wildfire in the Colorado Front Range, USA, Earth Surface Processes and Landforms, 38, 1049-1053, 2013.

Wolf, M., Lehndorff, E., Wiesenberg, G. L. B., Stockhausen, M., Schwark, L., and Amelung, W.: Towards reconstruction of past fire regimes from geochemical analysis of charcoal, Organic Geochemistry, 55, 11-21, 2013.

Wood, P. J. and Armitage, P. D.: Biological effects of fine sediment in the lotic environment, Environmental Management, 21, 203-217, 1997.

Zimmerman, A.: Abiotic and microbial oxidation of laboratory-produced black carbon (biochar), Environmental Science & Technology, 44, 1295-1301, 2010.

Zimmerman, A. R. and Gao, B.: The Stability of Biochar in the Environment. In: Biochar and Soil Biotia, Ladygina, N. and Rineau, F. (Eds.), CRC Press Taylor and Francis Group, Boca Raton, FL, 2013.

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, Limnology and Oceanography: Methods, 9, 140-140, 2011.

Table 1. Site characteristics (%C, %N, C:N, C stock) of forest floor, 0-5 cm soils 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	C stock (tC * ha^{-1})
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)

Claudia 4/7/2015 6:30 AM
Deleted: litter

Claudia Boot 4/4/2015 5:42 PM
Deleted: intensity

Claudia 4/2/2015 10:12 PM
Deleted:

Claudia Boot 4/4/2015 5:42 PM
Deleted: intensit

Claudia Boot 4/4/2015 5:42 PM
Deleted: y

Claudia 4/7/2015 6:30 AM
Deleted: litter

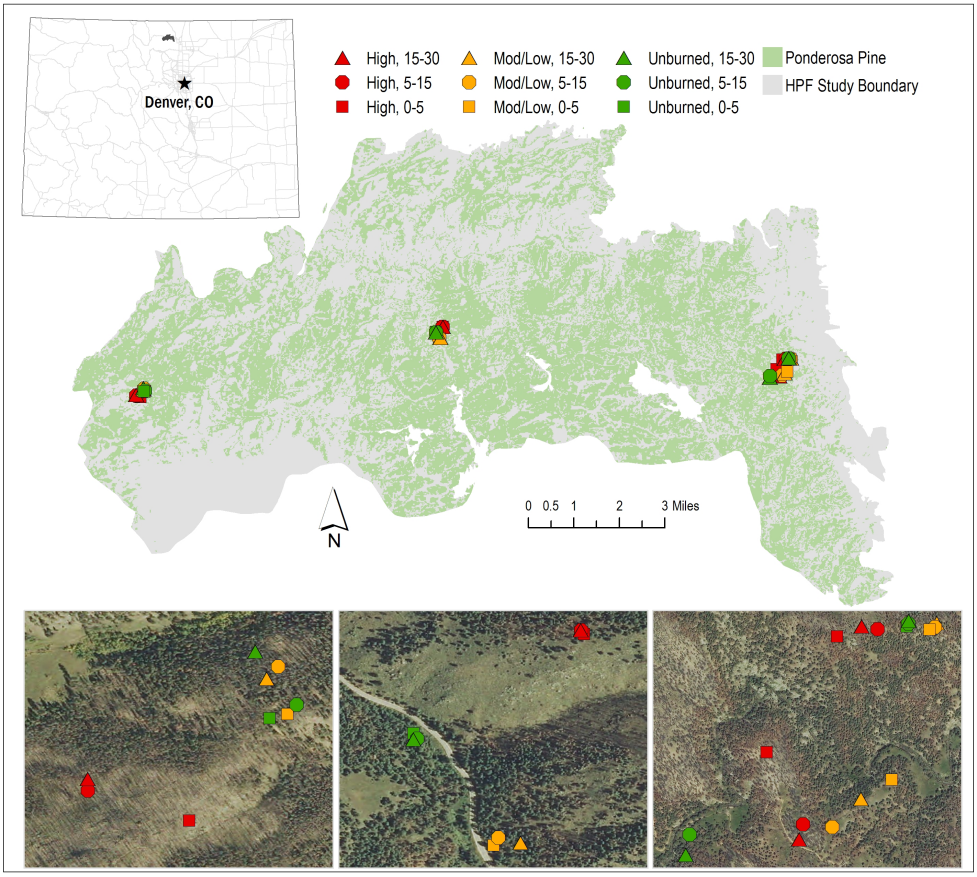


Figure 1. Location and classification (burn severity, and slope) of study sites (n=36) in the dominant Ponderosa pine vegetation highlighted in green within the High Park Fire burn area.

Claudia 4/2/2015 10:25 PM
Deleted: intensity

Claudia 4/2/2015 10:27 PM
Deleted:

Claudia Boot 4/4/2015 6:19 PM
Deleted: with

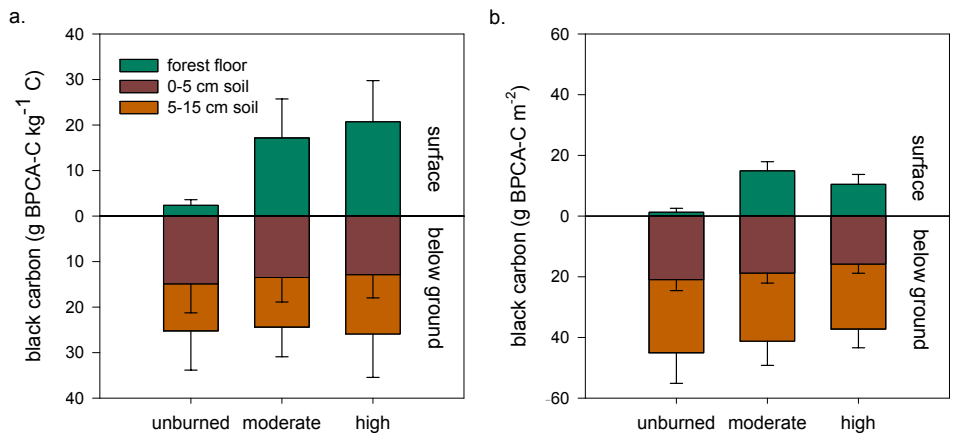


Figure 2. Distribution of black carbon in Ponderosa forest floor in (a.) g BPCA-C kg^{-1} C, and (b.) g BPCA-C * m^{-2} in forest floor (n=12), 0-5 cm (n=12), 5-15 cm (n=12) soils illustrating the significant differences in unburned versus moderately burned forest floor (p<0.001), highly burned forest floor (p<0.001), and unburned forest floor versus 0-5 cm soils (p<0.001) and 5-15 cm soils (p<0.001).

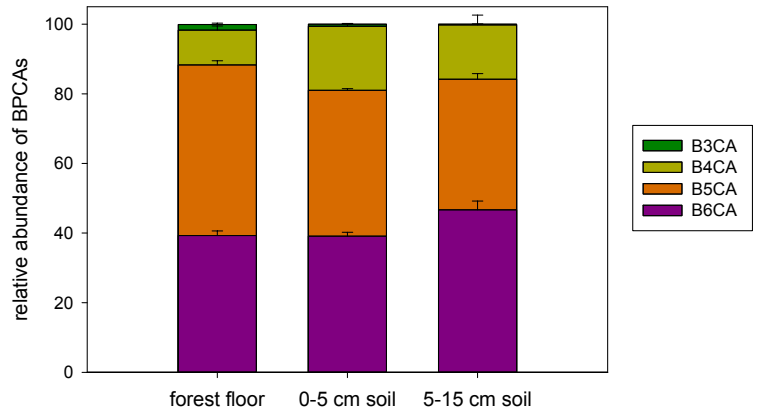
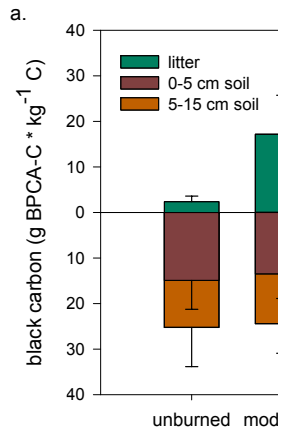


Figure 3. Distribution of BPCAs in each layer (n=36 per layer) illustrating greater relative abundance of B6CA in 5-15 cm soil versus 0-5 cm soil (p <0 .001) and forest floor (p<0.001).

Claudia 4/7/2015 8:10 AM

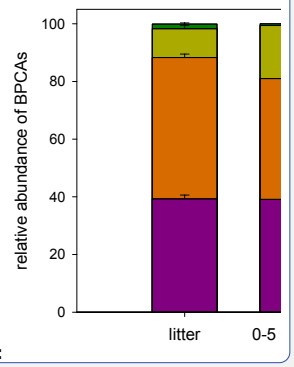


Deleted:

Claudia 4/7/2015 6:30 AM

Deleted: litter...orest floor in (a.) g ... [46]

Claudia Boot 4/8/2015 10:20 AM



Deleted:

Claudia 4/2/2015 10:21 PM

Deleted: 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)...elative abundanc ... [47]

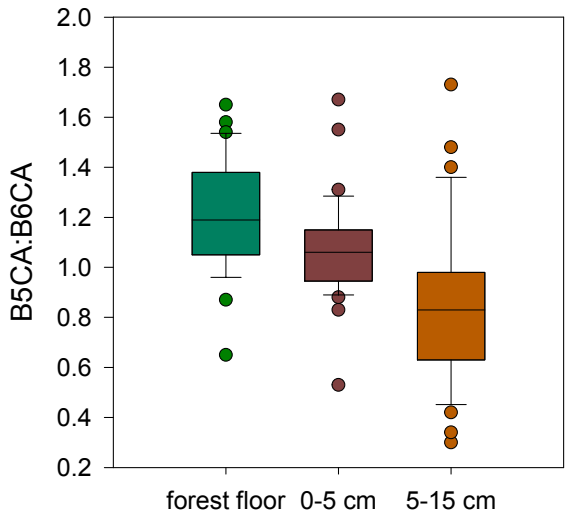


Figure 4. Ratio of B5CA to B6CA from 0.2 to 2.0, illustrating an increasing amount of B6CA and decreasing amount of B5CA with increasing soil depth (n=12 per layer), and significant difference between forest floor ratio and 5-15 cm ratio ($p<0.001$).

Claudia Boot 4/8/2015 11:45 AM
Deleted: ... [48]

Supplemental Information

Bulk Density Determination

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 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.

BPCA method validation

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. The laboratory biochar was derived from beetle-killed pine sourced from the CLP drainage combusted at approximately 400 to 500 °C and ground to a fine texture. The BPCA method validation with biochar-amended soils generated a linear relationship among the samples (BPCA-C = -1.506 + (0.89 * % 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 method was robust for quantifying BC and progressed with field-based sample collections.

Claudia Boot 4/8/2015 9:29 AM
Deleted: Millet seed b

Claudia Boot 4/8/2015 9:29 AM
Deleted: d

Claudia Boot 4/8/2015 9:29 AM
Deleted: d

Claudia Boot 4/8/2015 9:29 AM
Deleted:

Claudia Boot 4/8/2015 9:29 AM
Formatted: Indent: First line: 0.25"

Claudia 4/2/2015 11:11 PM
Formatted: Font:Bold, Not Italic

Table S1. Results of mixed model evaluating the effects of layer, burn severity, and slope on C and N values and bulk density presented with degrees of freedom (df) and p-values.

effect	df	log %C	log %N	C:N	log C stock (g C m^{-2})	bulk density
slope	2	0.306	0.872	**0.009**	0.774	0.927
burn	2	**0.002**	0.135	**<0.001**	0.080	0.796
layer	2	**<0.001**	**<0.001**	**<0.001**	**<0.001**	0.109
slope x burn	4	0.917	0.746	0.838	0.671	0.691
slope x layer	4	0.077	0.051	0.725	0.672	0.617
burn x layer	4	**<0.001**	**0.005**	**<0.001**	0.284	0.792
slope x burn x layer	8	0.093	0.169	0.685	0.534	0.875

Table S2. Results of Tukey's post-hoc comparisons evaluating the source of significant differences in %C, %N, C:N and C stocks by burn severity, layer, slope and the interaction terms presented as adjusted p-values.

post hoc comparisons	log % C	log % N	C:N	log C stock (g C m^{-2})
high vs. unburned	**0.001**	0.132	**<0.001**	0.320
moderate vs. unburned	0.371	0.835	**<0.001**	0.708
high vs. moderate	**0.029**	0.318	**0.004**	0.069
0-5 cm vs. forest floor	**<0.001**	**<0.001**	**<0.001**	**<0.001**
5-15 cm vs. forest floor	**<0.001**	**<0.001**	**<0.001**	**<0.001**
0-5 cm vs. 5-15 cm	**<0.001**	**<0.001**	0.703	0.696
0-5 vs. 5-15 degrees	0.998	0.941	**0.028**	0.755
0-5 vs. 15-30 degrees	0.932	0.984	**0.012**	0.915
5-15 cm vs. 15-30 degress	0.947	0.864	0.916	0.944
forest floor: unburned vs. moderate	**0.009**	0.968	**<0.001**	0.217
forest floor: unburned vs. high	**<0.001**	**0.004**	**<0.001**	0.400
forest floor: moderate vs. high	**<0.001**	**0.006**	**<0.001**	**0.009**
0-5 cm: unburned vs. moderate	0.631	0.978	0.471	0.938
0-5 cm: unburned vs. high	0.947	0.513	1.000	0.805
0-5 cm: moderate vs. high	0.166	0.376	0.448	0.582
5-15 cm: unburned vs. moderate	0.662	0.448	0.999	0.840
5-15 cm: unburned vs. high	0.947	0.999	0.674	0.706
5-15 cm: moderate vs. high	0.836	0.399	0.628	0.968

Claudia 4/7/2015 7:44 AM
Deleted: three-way ANOVA

Claudia Boot 4/8/2015 9:19 AM
Deleted:

Claudia 4/7/2015 7:44 AM
Deleted: intensity

Claudia 4/7/2015 7:43 AM

response variable	df	f-v
slope	2	1.(
burn	2	**7.**
layer	2	**27**
slope x burn	4	0.2
slope x layer	4	0.8
burn x layer	4	**5.**
slope x burn x layer	8	0.(

Deleted:

Claudia Boot 4/8/2015 9:16 AM
Deleted: ... [49]

Claudia Boot 4/8/2015 9:17 AM
Deleted: , not significant (ns), not tested (nt)

Claudia 4/7/2015 7:43 AM

post hoc comparisons	(
high vs. unburned	
moderate vs. unburned	
high vs. moderate	
0-5 cm vs litter	
5-15 cm vs litter	
0-5 cm vs 5-15 cm	
0-5 vs 5-15 degrees	
0-5 vs 15-30 degrees	
5-15 cm vs 15-30 degress	
litter: unburned vs. moderate	
litter: unburned vs. high	
litter: moderate vs. high	
0-5 cm: unburned vs. moderate	
0-5 cm: unburned vs. high	
0-5 cm: moderate vs. high	
5-15 cm: unburned vs. moderate	
5-15 cm: unburned vs. high	
5-15 cm: moderate vs. high	

Deleted:

Claudia Boot 4/8/2015 9:16 AM
Deleted:

Table S3. Results of mixed model evaluating the effects of layer, burn severity and slope on BPCA-C concentration and stocks presented as degrees of freedom (df) and p-values.

effect	df	BPCA C (g kg^{-1} C)	log BPCA C stock (g BPCA-C m^{-2})
slope	2	0.446	0.801
burn	2	**0.007**	**0.012**
layer	2	0.610	**<0.001**
slope x burn	4	0.191	0.853
slope x layer	4	0.740	0.829
burn x layer	4	**<0.001**	**<0.001**
slope x burn x layer	8	0.545	0.679

Table S4. Results of Tukey's post-hoc comparisons evaluating the source of significant differences in BPCA-C concentration and stocks by burn severity, layer, and the burn by layer interaction presented as adjusted p-values.

post hoc comparisons	BPCA C (g BPCA-C kg^{-1} C)	log BPCA C stock (g BPCA-C m^{-2})
high vs. unburned	**0.005**	0.135
moderate vs. unburned	0.072	**0.009**
high vs. moderate	0.576	0.408
0-5 cm vs. forest floor	0.980	**<0.001**
5-15 cm vs. forest floor	0.734	**<0.001**
0-5 cm vs. 5-15 cm	0.615	0.814
unburned: 0-5 cm vs. forest floor	**<0.001**	**<0.001**
unburned: 5-15 cm vs. forest floor	**0.004**	**<0.001**
unburned: 0-5 cm vs 5-15 cm	0.711	0.882
moderate: 0-5 cm vs. forest floor	0.418	0.484
moderate: 5-15 cm vs. forest floor	0.085	0.847
moderate: 0-5 cm vs 5-15 cm	0.646	0.817
high: 0-5 cm vs. forest floor	**0.023**	0.172
high: 5-15 cm vs. forest floor	**0.027**	0.162
high: 0-5 cm vs. 5-15 cm	0.998	0.999
forest floor: unburned vs. moderate	**<0.001**	**<0.001**
forest floor: unburned vs. high	**<0.001**	**<0.001**
forest floor: moderate vs. high	0.445	0.330
0-5 cm: unburned vs. moderate	0.874	0.999
0-5 cm: unburned vs. high	0.761	0.696
0-5 cm: moderate vs. high	0.974	0.709
5-15 cm: unburned vs. moderate	0.845	0.989
5-15 cm: unburned vs. high	0.986	0.948
5-15 cm: moderate vs. high	0.742	0.983

Claudia Boot 4/8/2015 9:18 AM
Deleted:

Claudia Boot 4/8/2015 9:25 AM
Deleted: three-way

Claudia 4/7/2015 7:44 AM
Deleted: ANOVA

Claudia 4/7/2015 7:45 AM
Deleted: intensity

Claudia Boot 4/8/2015 9:20 AM
Deleted:

Claudia 4/7/2015 7:43 AM

response variable	df	f-\
slope	2	
burn	2	
layer	2	
slope x burn	4	
slope x layer	4	
burn x layer	4	
slope x burn x layer	8	

Deleted:

Table S5. Results of mixed model evaluating the effects of burn, layer and their interaction on the relative abundances of B6CA, B5CA, B4CA and the ratio of B5CA:B6CA presented as degrees of freedom (df) and adjusted p-values.

effect	df	B6CA	B5CA	B4CA	B5CA:B6CA
burn	2	0.902	0.939	0.401	0.805
layer	2	**<0.001**	**<0.001**	**<0.001**	**0.002**
burn x layer	4	0.079	0.288	0.543	0.053

Table S6. Tukey's Post hoc comparisons among layers and burn by layer interaction for relative abundance of B6CA, B5CA, B4CA and the ratio of B5CA:B6CA presented as the adjusted p-values.

post hoc comparisons	B6CA	B5CA	B4CA	B5CA:B6CA
0-5 cm vs. forest floor	0.997	**<0.001**	**<0.001**	0.115
5-15 cm vs. forest floor	**<0.001**	**<0.001**	0.148	**0.001**
0-5 cm vs. 5-15 cm	**<0.001**	**0.037**	**0.002**	0.176

Deleted:

post hoc comparisons
high vs. unburned
moderate vs. unburned
high vs. moderate
0-5 cm vs litter
5-15 cm vs litter
0-5 cm vs 5-15 cm
unburned: 0-5 cm vs litter
unburned: 5-15 cm vs litter
unburned: 0-5 cm vs 5-15 c
moderate: 0-5 cm vs litter
moderate: 5-15 cm vs litter
moderate: 0-5 cm vs 5-15 c
high: 0-5 cm vs litter
high: 5-15 cm vs litter
high: 0-5 cm vs 5-15 cm
litter: unburned vs. modera
litter: unburned vs. high
litter: moderate vs. high
0-5 cm: unburned vs. mode
0-5 cm: unburned vs. high
0-5 cm: moderate vs. high
5-15 cm: unburned vs. moc
5-15 cm: unburned vs. high
5-15 cm: moderate vs. high

Claudia Boot 4/8/2015 9:23 AM

Deleted: ... [50]

Claudia 4/7/2015 7:45 AM

Deleted: B4CA:B6CA and

Claudia 4/7/2015 7:43 AM

response variable	df	f-
burn	2	
layer	2	
burn x layer	4	

Deleted:

Claudia 4/7/2015 7:46 AM

Deleted: (litter, 0-5 cm soils, and 5-15 cm soils)

Claudia 4/7/2015 7:43 AM

post hoc comparisons	diff. r
0-5 cm vs litter	
5-15 cm vs litter	
0-5 cm vs 5-15 cm	

Deleted:

Claudia Boot 4/8/2015 11:44 AM

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