

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

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32 **Abstract**

33 Biomass burning produces black carbon (BC), effectively transferring a fraction of the
34 biomass C from an actively cycling to a passive C pool, which may get stored in the soil. Yet
35 the timescales and mechanisms for incorporation of BC into the soil profile are not well
36 understood. The High Park Fire (HPF), which took place in northwestern Colorado in the
37 summer of 2012, provided an opportunity to study the effects of both fire severity and
38 geomorphology on properties of carbon (C), nitrogen (N), and BC in the Cache La Poudre
39 River drainage. We sampled montane Ponderosa pine forest floor, 0-5 cm soils, and 5-15
40 cm soils four months post-fire in order to examine the effects of slope and burn severity on
41 %C, C stocks, %N and BC. We used the benzene polycarboxylic acid (BPCA) method for
42 quantifying BC. With regard to slope, we found that steeper slopes had higher C:N than
43 shallow slopes, but that there was no difference in BPCA-C content or stocks. BC content
44 was greatest in the forest floor in burned sites (19 g BPCA-C kg⁻¹ C), while BC stocks were
45 greatest in the 5-15 cm subsurface soils (23 g BPCA-C m⁻²). At the time of sampling,
46 unburned and burned soils had equivalent BC content, indicating none of the BC deposited
47 on the land surface post-fire had been incorporated into either the 0-5 cm or 5-15 cm soil
48 layers. The ratio of B6CA:total BPCAs, and index of the degree of aromatic C condensation,
49 suggested that BC in the 5-15 cm soil layer may have been formed at higher temperatures
50 than the forest floor and 0-5 cm soils. Total BC soil stocks were relatively low compared to
51 other fire-prone grassland and boreal forest systems, indicating most of the BC produced in
52 this system is likely lost from the system, either through erosion events, degradation or
53 translocation to deeper soils. Future work examining mechanisms for BC losses from the
54 forest soil will be required for understanding the role BC plays in the global carbon cycle.
55

56 **1. Introduction**

57 While pyrogenic or black carbon (BC) is now recognized as a ubiquitous soil carbon (C)
58 fraction it is one of the least understood components of the terrestrial C cycle. Every year,
59 fire burns approximately $10\text{-}15 \times 10^6$ ha of boreal and temperate forest and more than 500
60 $\times 10^6$ ha of tropical and subtropical forests and savannas (Goldammer and Crutzen, 1993;
61 Knicker, 2011), during which 0.12 to 9.5% of the burned biomass is converted to BC
62 (Forbes et al., 2006). Black C is utilized by soil microbes, but at a slow rate (Santos et al.,
63 2012). Thus it generally resides in the soil for a long time (from centuries to millennia)
64 (Singh et al., 2012), acting as a long-term C sink, with a potential negative feedback on
65 climate warming. However, BC stocks in soils are not only related to BC production rate
66 and decomposition, but may also be lost through runoff, leaching or burning (Czimczik and
67 Masiello, 2007; Foereid et al., 2011), and thus BC stocks are strongly dependent on surface
68 topography and soil physical-chemical environment (Bird et al., 2015; Knicker, 2011).

69 BC persistence and dynamics in soil seem to be controlled by mechanisms similar to
70 those that control soil organic matter dynamics including inherent chemical recalcitrance
71 and organo-mineral interactions (Knicker, 2011). Persistent BC particles in soils are
72 composed of a refractory, aromatic core and a reactive, oxidized patina (Keiluweit et al.,
73 2010; Lehmann et al., 2005) characterized by carbonyl and carboxyl functionalities (Cheng
74 et al., 2008; Cheng et al., 2006). The degree of condensation of the aromatic core has been
75 shown to be quite variable (McBeath and Smernik, 2009; Wiedemeier et al., 2015d), but
76 can be broadly characterized as dominated by C in condensed aromatic rings resistant to
77 decomposition (Baldock and Smernik, 2002). Besides its inherent chemical recalcitrance,
78 BC stabilization in soils likely occurs through bonding to minerals, which is thought to be
79 the most persistent mechanism of SOM stabilization (von Lutzow et al., 2006). The
80 presence of carboxyl functionalities on BC surfaces provides 'teeth' available to chelate soil
81 aluminum and iron, creating BC-mineral complexes that are highly refractory to microbial
82 decay and have longer mean residence times than non mineral-associated BC (Christensen,
83 1996; von Lutzow et al., 2006).

84 In order to become stabilized in soils, BC must first be transferred from burned surface
85 material to the subsurface, and the process of incorporation will be strongly related to
86 surface topography. The shape of a landscape and propensity for erosion versus deposition

87 is dependent upon several variables including bedrock composition, slope, elevational
88 gradients in temperature and precipitation, and disturbance history such as the frequency
89 of wildfires. While the strong relationship between geomorphology and soil
90 erosion/sediment transport is fairly well understood (Ritchie and McCarty, 2003; Slater
91 and Carleton, 1938), the relationship between soil erosion and fate of different components
92 of SOM that are eroded, including BC, are relatively unknown (Bird et al., 2015; Rumpel et
93 al., 2006).

94 The difficulty in measuring BC contributes to our limited understanding of its transport
95 processes and function in the global C cycle. Because BC exists along a continuum of
96 combustion products, from charred biomass to soot, with differing physical and chemical
97 features, no single method can accurately quantify total BC content (Hammes et al., 2007;
98 Masiello, 2004). Visual counts of charcoal, resistance to oxidation methods, nuclear
99 magnetic resonance spectroscopy (NMR) or the quantification of BC-specific molecular
100 markers (e.g., benzene polycarboxylic acids (BPCAs)) have each been employed for
101 quantification of BC. While each approach has advantages and disadvantages, the BPCA
102 method has been shown to yield conservative estimates of BC with charred inputs and
103 more consistent results than many other quantification methods (Hammes *et al.* 2007).
104 Moreover, the BPCA method yields additional information about BC quality related to its
105 degree of aromatic condensation and aromaticity (Schneider et al., 2010; Schneider et al.,
106 2013; Wiedemeier et al., 2015a; Ziolkowski et al., 2011).

107 A few estimates exist of BC production after fire (Santín et al., 2012), as well as of BC
108 stocks in soils for different ecosystems (Bird et al., 1999; Cusack et al., 2012; Schmidt et al.,
109 2002). Yet, estimates of BC production and losses are not balanced (Czimczik and Masiello,
110 2007; Rivas et al., 2012), clearly identifying our lack of understanding and the need for a
111 full accurate accounting of BC dynamics after fire at the watershed level.

112 Between June 9th-24th, 2012, the High Park fire (HPF) burned more than 35,000 ha in
113 northern Colorado along the Cache la Poudre (CLP) River in an area dominated by
114 ponderosa pine (*Pinus ponderosa*) (Figure 1). The aims of this work were to: 1. determine
115 the C, and BC stocks, and the proportion of C that was BC, in Ponderosa pine forest floor
116 and soils following the HPF; 2. examine the effects of burn severity and landscape slope on
117 soil C, N and proportion of BC; and 3. use the distribution of individual BPCAs to

118 understand the degree of condensation of BC through the soil profile. We expected that BC
119 stocks would be the greatest in high burn severity sites, followed by moderate, then
120 unburned sites, and that the hillslope would have the opposite effect, with lowest BC stocks
121 on the steepest slopes, and greatest BC stocks on shallow slopes. We anticipated that BC
122 and C stocks would be greater in the forest floor than in soils, and that soil C stocks would
123 be diminished in high burn severity surface soils due to combustion during fire. We also
124 expected that the molecular characteristics of BC would change with depth related to their
125 degree of condensation.

126

127 **2. Materials and Methods**

128 *2.1 Experimental Design and Site Identification*

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

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

142 Our study was a fully factorial, randomized block design with four replicate blocks for
143 all treatments plots, including three levels of burn severity (unburned, moderate burn, high
144 burn) and three slopes (0-5, 5-15 and 15-30 degrees), for a total of 36 plots. We opted to
145 constrain the study by slope rather than landscape position (e.g. hilltop versus valley
146 location of flat surface) in order to constrain study site criteria to public lands within the
147 patchy distribution of fire-impacted sites of Ponderosa pine vegetation on difficult to access
148 terrain. Geographic Information System (GIS) layers of land ownership, slope, fire intensity,

149 and burn severity were obtained prior to site location. Potential sampling areas were
150 chosen in state or federal land in areas of homogenous vegetation stands where all slope
151 classes and fire classes were present within a close distance (Figure 1). Ground truthing
152 was subsequently done to locate each specific slope and burn severity sampling treatment
153 plot. Slopes were determined using a clinometer. Areas were classified as high burn when
154 the fire had burned the entire tree and no needles or small branches remained, the litter
155 layer was consumed in the fire and there were some small pieces of charcoal throughout
156 the surface layer. Moderate burn areas had ground fire and some crown scorch, but
157 crowns did not burn, at least some needles remained on the trees and the litter layer
158 remained on the forest floor with some small pieces of charcoal. Unburned areas had no
159 evidence of ground fire and no evidence of burned material on the ground surface.

160 **insert Figure 1**

161 *2.2 Forest Floor and Soil Collection*

162 Soil and forest floor samples were collected between October and November of 2012.
163 At each of the 36 experimental plots, forest floor and soils were collected from within a 20
164 by 20 cm wooden frame, and frame GPS coordinates were recorded. The forest floor layer
165 was sampled first including any litter plus organic soils down to the mineral layer, and then
166 the soil was excavated with a hand shovel separately for the 0-5 cm and 5-15 cm depth.
167 Due to the high surface variability, 4 additional forest floor samples and 3 surface (0-5cm)
168 soil samples were collected at each site, positioning the frame orthogonally to a distance of
169 2.5 m from the original position. All forest floor and surface soil samples were pooled by
170 plot.

171 Due to the extreme rockiness at all of the sampling locations soil bulk density was
172 determined using pit excavation separately for each depth layer (Page-Dumroese et al.,
173 1999). The volume of the pit was determined using volume displacement with millet seed
174 (detailed description in Supplemental Information). Soil and forest floor samples were
175 transported to the lab and stored at 4°C until processing.

176

177 *2.3 Forest Floor, Soil Pretreatment and Elemental Analyses*

178 In the laboratory, forest floor samples were weighed field-moist and a subsample of
179 each was dried at 105°C for 48 hours for dry weight correction. Forest floor samples were

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

185 Soil samples were weighed field-moist and a subsample of each was dried at 105°C for
186 48 hours for dry weight correction. Bulk density of each soil depth was calculated as the
187 weight of oven dry soil with rock removed (Throop et al., 2012) divided by the volume for
188 the depth determined by millet with rock volume removed. Soils were sieved air dry to 2
189 mm and a subsample was oven dried (105°C) and finely ground. All the ground, dry, forest
190 floor and soil samples were analyzed for total C and N by an elemental analyzer (LECO
191 CHN-1000; LECO Corporation, St. Joseph, MI, USA), and for BC by the BPCA method as
192 described below.

193

194 *2.4 BPCA Analyses*

195 The BPCA method converts condensed aromatic structures to single aromatic rings
196 with variable numbers of carboxylic acid moieties, and a greater degree of condensation
197 (i.e. number of fused rings) correlates with a greater number of carboxylic acid moieties on
198 the individual BPCAs such that more condensed structures result in greater relative
199 abundance of B6CAs and the least condensed BC would result in a greater proportion of
200 B3CAs (Glaser et al., 1998; Wiedemeier et al., 2015a; Ziolkowski et al., 2011). Black C was
201 determined on all forest floor and soil samples using high performance liquid
202 chromatography (HPLC) equipped with a photo diode array detector to quantify benzene
203 polycarboxylic acids (BPCA) as described by (Wiedemeier et al., 2013). The BPCA method
204 was validated with biochar-amended soils from the field site (see Supplemental
205 Information). Briefly, 50-150 mg of finely ground, oven dried sample was digested with
206 70% nitric acid for 8 hours at 170°C. The solution was filtered with ashless cellulose filters,
207 an internal reference standard of phthalic acid was added to the solution, and the filtrate
208 was cleaned by cation exchange resin and freeze-dried. The freeze-dried sample was re-
209 dissolved in HPLC grade water. The re-dissolved solution containing the BPCAs was
210 separated with a reversed stationary phase column (Waters X-Bridge C18, 3.5 um particle

211 size, 2.1 x 150 mm) using standard gradient conditions. Individual BPCAs were quantified
212 with using a five-point calibration from standard solutions of benzenetricarboxylic acids
213 (1,2,3-B3CA/hemimellitic acid, 1,2,4-B3CA/trimellitic acid, 1,3,5-B3CA/trimesic acid),
214 benzenetetracarboxylic acid (1,2,4,5-B4CA/pyromellitic acid), benzenepentacarboxylic
215 acid (B5CA), and benzenhexacarboxylic acid (B6CA/mellitic acid). The B4CA standards
216 that are not commercially available (1,2,3,4-B4CA/prehenitic acid, and 1,2,3,5-
217 B4CA/mellophanic acid) were identified by their ultraviolet adsorption spectra and
218 quantified using the calibration for 1,2,4,5-B4CA (Yarnes et al. 2011). Previous attempts to
219 calculate a BPCA-C to BC conversion factor have resulted in values that range from 2.27 to
220 5, and have been difficult to reproduce (Brodowski et al., 2005; Glaser et al., 1998;
221 Ziolkowski et al., 2011). Thus, to simplify empirical comparisons we report values as BPCA-
222 C, either as a proportion of total C or as a stock.

223

224 *2.5 Data Analyses*

225 The effects of layer (forest floor, 0-5 cm soil, 5-15 cm soil, n=4 per layer), slope (0-5°, 5-
226 15°, 15-30°, n=4 per slope) burn severity (unburned, moderate burn, high burn, n=4 per
227 severity) and all interaction terms on each response variable (soil C, soil N, BPCA C stock,
228 BPCA C as a proportion of total C, and relative abundances of B4CA, B5CA, B6CA and
229 B5CA:B6CA ratio) were compared using the SAS mixed procedure (proc mixed); fixed
230 variables were layer, slope and severity, and block and core were designated as random
231 effects. Post-hoc analysis for significant terms was conducted using Tukey's test. When
232 necessary, dependent variable data were log-transformed (%C, %N, C stock, BPCA-C g m⁻²)
233 to meet assumptions of equal variance and normality, which were assessed with
234 Studentized residual diagnostic plots. The null hypothesis, that the independent factor had
235 no effect, or that no linear correlation existed between variables, for all tests was evaluated
236 at $\alpha < 0.05$. Analyses were run using SAS 9.4.

237

238 **3. Results**

239 *3.1 Percent and Stocks of C and N in Forest floor and Soil*

240 Values for %C ranged from 29% in the forest floor to 0.9% C in the 5-15 cm soil layer,
241 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

242 the forest floor to 13 in 5-15 cm soil. We tested for effects of layer, burn severity, slope and
243 their interactions and found that the main effects were distinct for each response variable
244 (%C, %N and C:N). Effects of burn severity ($p=0.002$) and layer (<0.001) on %C, could not
245 be independently assessed because the burn \times layer interaction was also significant
246 ($p<0.001$, Table S1). Only layer had an effect on %N ($p<0.001$), while the C:N ratio was
247 affected by slope ($p=0.009$), burn intensity ($p<0.001$), layer ($p<0.001$) and in interaction
248 ($p<0.001$).

249 **insert Table 1**

250 Post hoc comparisons (Table S2) confirmed expected decreases in %C and %N from
251 forest floor to 5-15 cm soil ($p<0.001$ for each successive layer), along with a decreasing C:N
252 from forest floor to 0-5 cm soil ($p<0.001$) and with no change between 0-5 cm and 5-15 cm
253 soil ($p=0.703$). The burn severity \times layer interaction term illustrated that the effects of burn
254 were confined to the forest floor layer for %C and C:N. Within the forest floor layer,
255 unburned sites had greater %C than moderately burned ($p=0.009$) or highly burned sites
256 ($p<0.001$), and moderately burned sites also had greater %C than highly burned sites
257 ($p<0.001$). For the C:N ratio the pattern was the same: C:N was widest in unburned sites
258 which decreased significantly at moderately burned sites ($p<0.001$) and further still at
259 highly burned sites ($p<0.001$). Interestingly, slope also had an effect on the C:N. Post hoc
260 comparisons indicated that C:N on 0-5 slopes was lower than 5-15 degree slopes ($p=0.028$)
261 and the C:N on 0-5 degree slopes was significantly lower than 15-30 degree slopes
262 ($p=0.012$), while the 5-15 and 15-30 degree slopes were not different ($p=0.916$).

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

268

269 *3.2. Benzene Polycarboxylic Acid-C in forest floor and soil*

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

273 forest floor, to 40.0 g kg⁻¹ OC in highly burned forest floor, and for stocks from 0.1 g m⁻² in
274 unburned forest floor to 19.52 g m⁻² in moderately burned forest floor. In soils,
275 concentration ranged from 2.86 g kg⁻¹ OC in moderately burned 0-5 cm soil to 33.83 g kg⁻¹
276 OC in 5-15 cm highly burned soils, and stocks ranged from 2.92 g m⁻² in highly burned 0-5
277 cm soils to 96.66 g m⁻² in unburned 5-15 cm soil.

278 Burn severity and layer were the main effects on the concentration and stock of BPCA-C
279 (Figure 2, Table S3). Results of a mixed model (slope, burn severity, layer and interactions)
280 indicated that there was no significant effect of slope either independently (p = 0.446) or in
281 interaction (slope × burn p=0.191, slope × layer p=0.740) on BC concentration. Mean
282 values for BPCA-C stock did decrease with increasing slope in moderately burned forest
283 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
284 +/- 4.3 g m⁻²), however the trend was not significant due to high variability. The
285 independent effects of burn severity (concentration: p=0.007, stock: p=0.012), and layer
286 (concentration: p=0.610, stock p<0.001) could not be interpreted independently as the
287 interaction of burn severity and layer was also significant (concentration and stock: burn ×
288 layer p<0.001).

289 Post hoc comparisons indicated that within the forest floor layer, high and moderately
290 burned material contained significantly more BPCA-C, both by concentration and stock,
291 than unburned material (Table S4, p<0.001 for both). Within the 0-5 and 5-15 cm layers,
292 there was no statistically significant difference in BPCA-C concentration or stock regardless
293 of burn severity. Within unburned layers, 0-5 and 5-15 cm soils had significantly greater
294 amounts of BPCA-C than forest floor, both by concentration (p<0.001, p=0.004,
295 respectively) and stock (p<0.001 for both). Within high burn severity, forest floor and soil
296 BPCA-C stocks and concentrations yielded distinct results: the amount of C that was BPCA-
297 C was greater in the forest floor than 0-5 and 5-15 cm soils (p=0.023, p=0.027,
298 respectively), whereas the stock of BPCA-C was not significantly different in the high burn
299 among forest floor and soil layers.

300 **insert Figure 2**

301 We expected that the layer (forest floor, 0-5 cm soil, 5-15 cm soil) and burn severity
302 may contribute to the distribution of BPCAs with BC formed at different temperatures
303 (B5CA:B6CA), or by a higher proportion of more condensed C (B6CA:total BPCAs) with

304 increasing soil depth. Overall, the bulk of BPCAs were B5CA and B6CA varieties, together
305 making up approximately 80% of the total BPCA-C. The B4CAs were the next most
306 abundant (10-20%) and the B3CAs were less than 3%. Results from statistical analyses
307 indicated that 'layer' was the main effect on the distribution of BPCAs ($p < 0.001$, Table S5).
308 Layer also had a significant effect on the ratio of B5CA to B6CA, ($p = 0.002$, Table S5, Figure
309 4). Post hoc comparisons were used to evaluate the relative abundance of each BPCA by
310 layer: the proportion of B6CA was greater in the 5-15 cm soil than both 0-5 cm soil and
311 forest floor layers ($p < 0.001$); B5CA was greater in the forest floor than 0-5 cm soil and 5-15
312 cm soils ($p < 0.001$ for both), and greater in 0-5 cm soils than 5-15 cm soils ($p = 0.037$); B4CA
313 was greater in 0-5 cm soil than in forest floor ($p < 0.001$), and 5-15 cm soil ($p = 0.002$), with
314 no difference in forest floor and 5-15 cm soil ($p = 0.148$). The ratio of B5CA:B6CA decreased
315 with depth due to both decreasing amounts of B5CA and increasing amounts of B6CA. The
316 B5CA:B6CA ratio was significantly greater in the forest floor than 5-15 cm soils ($p = 0.001$)
317 (Figure 3, Table S6)).

318 **insert Figure 3**

319

320 **4. Discussion**

321 Our primary objective was to determine the C socks, BPCA-C stocks, and the proportion
322 of C that was BPCA-C in Ponderosa pine forest floor and soils following the HPF. BC can
323 account for 1% to 45% of the soil organic C depending upon fire return interval (Czimczik
324 et al., 2005; Saiz et al., 2014), ecosystem type, soil mineralogical properties (Preston and
325 Schmidt, 2006) other factors that influence OC stabilization (Knicker, 2011), as well as the
326 method used for quantification. Estimates of BC content based on BPCA-measurements are
327 generally lower than those made with chemical- thermal- or photo-oxidation based
328 measurements or with NMR (Preston and Schmidt, 2006). Only a few studies have
329 estimated the amount of BC in forest soils using the BPCA method with values that range
330 10 to 60 g/kg organic C and 0-80 g/m² (Czimczik et al., 2003; Czimczik et al., 2005;
331 Rodionov et al., 2006). Excluding unburned forest floor samples, we found values within
332 this range, averaging 14 (± 7) g BPCA-C kg⁻¹ C, and 19 (± 5) g BPCA-C per m². It is important
333 to note that BPCAs are markers for BC, and their total amount is two to five times lower

334 than the amount of BC. This should be taken into consideration when comparing BPCA
335 estimates with BC distribution values in systems that have been assessed with different
336 methods (Brodowski et al., 2005; Glaser et al., 1998; Ziolkowski et al., 2011).

337 We also aimed to determine how the slope of the landscape and burn severity would
338 influence the amount of BC in forest floor and soil layers following a major wildfire. We
339 found that neither slope nor burn severity had an effect on BC concentration in soils.
340 Interestingly, even the soils from unburned sites had an average BC content of 14 g BPCA-C
341 kg⁻¹ of C, suggesting a persistent BC pool from past fires. Within the forest floor layer,
342 however, unburned sites contained very low BPCA-C and moderate and highly burned sites
343 contained significantly more, averaging 18 g BPCA-C per kg of OC suggesting that the
344 majority of the BC remaining on the landscape after the HPF persisted in the forest floor
345 rather than moving into the surface soil four months post-fire.

346 We expected that during the interval between the HPF (June 2013), and sample
347 collection (October 2013), HPF-derived BC would have begun to move off of steeper slopes
348 during post-fire erosion events, resulting in lower BC deposits on steeper slopes. However,
349 we observed consistent BC content across slopes with the HPF-derived BC isolated to the
350 forest floor layer in both highly and moderately burned areas on a per unit C and per m²
351 basis. Although slope did not contribute to the landscape pattern of BC distribution over
352 the time period of our study, the summer of 2013 was particularly dry with very few high
353 intensity rain events (Wohl, 2013). Thus, slope may only become a contributing variable to
354 landscape-level post-fire BC distribution when there are precipitation events sufficient to
355 produce significant sediment movement. In addition, steeper slopes generally have
356 increased surface roughness in montane systems constraining overland sediment
357 movement (Wohl, 2013). We qualitatively examined photos of each of the collection sites
358 and noted increased surface roughness in some of the steeper replicates, thus increased
359 surface roughness is a plausible explanation for similar BPCA-C values on shallow vs.
360 steeper slopes.

361 The position of our sites on the landscape may have also contributed to the lack of effect
362 of slope on BC distribution. Because our aim was to address slope, rather than position, the
363 sites were not oriented in a consistent up- or downslope manner, thus some 0-5° sites are
364 located on hilltops and others at valley bottoms. In addition, the landscape position

365 influences the location of Ponderosa pine through elevational temperature and moisture
366 gradients (Peet, 1981). We focused on the Ponderosa pine because it is the dominant
367 vegetation in the drainage located on a variety of slopes, whereas consideration of hillslope
368 processes would require accounting for the differences in fire properties and BC inputs that
369 would likely result from grass or shrub dominated areas (DeBano, 2000).

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

379 Concentrations of post-fire BC have been shown to be highest in the surface of
380 moderately burned soils due to consumption of relict BC content in highly burned areas
381 (Czimczik et al., 2003). However, in our study, on a per unit C basis the amount of BC in
382 surface 0-5 cm soils was not distinguishable across burn intensities (~ 14 g BPCA-C kg^{-1}),
383 while on a per m^2 basis, moderately burned material had greater BC content (20 g BPCA-C
384 m^{-2}) than unburned material (17 g BPCA-C m^{-2}). The cumulative difference between
385 unburned and moderately burned material was driven by low BC content in the forest floor
386 layer at unburned sites. While the highly burned material did not contain significantly less
387 BC than the moderately burned material, it was also not significantly different from
388 unburned material, largely driven by cumulative losses from both the forest floor and 0-5
389 cm soil BC stocks. Essentially, the stocks of BC in unburned and highly burned sites are the
390 same, they are just distributed differently: the highly burned sites have greater BC stocks in
391 forest floor than soil, and the unburned sites have greater BC stocks in soil than forest floor
392 (Figure 2).

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

396 that eventually a proportion of the BC produced during the HPF will be introduced into the
397 soils and retained in the ecosystem. Given a fire return interval of ~ 70 years in Ponderosa
398 forests, and a mean residence time for BC stock in soils of approximately 300 years
399 (Hammes et al., 2008; Schmidt et al., 2011), using first order decay, we calculated that 2.4 g
400 m^{-2} , or 17% of the HPF fire-derived BC in forest floor ($\sim 14 \text{ g m}^{-2}$) would be transferred to
401 the 0-15 cm soil to maintain a steady state stock ($\sim 40 \text{ g m}^{-2}$). This calculation contains a
402 high degree of uncertainty; a greater residence time for BC would result in decreased
403 incorporation, and the reverse for a shorter residence time, and fires with different
404 properties will deposit different amounts of BC on the soil.

405 The estimate for BC incorporation described above is not meant to be used as
406 characteristic value for this ecosystem, but instead is meant to illustrate that the bulk of the
407 BC in this system likely moves off the surface, either through incorporation into deeper
408 soils, biotic or abiotic degradation, or export through erosion. BC incorporation at depth via
409 water flow and biotic infiltration processes stimulated by soil fauna, has been suggested to
410 be the prime mechanism by which BC is sequestered in the soil (Czimczik and Masiello,
411 2007), although we would have expected to see some increase in the BC content of surface
412 soils in burned sites if incorporation to deep soil was the dominant mechanism. An
413 additional alternative is loss of BC through biotic and abiotic degradation, as a proportion
414 of BC is known to be labile (Zimmerman, 2010), however that proportion is small (Stewart
415 et al., 2013; Zimmerman and Gao, 2013) and other mechanisms are most likely to
416 contribute to major loss pathways. Erosion rates in montane ecosystems post-fire can
417 increase up to three orders of magnitude depending on the severity of the fire and the
418 intensity of precipitation (Wagenbrenner and Robichaud, 2014). Erosion has been shown
419 to be important for BC distribution, as previous work has demonstrated approximately
420 50% of BC may be lost through erosion processes (Major et al., 2010; Rumpel et al., 2009).
421 While each of these loss mechanisms, degradation, downward translocation and erosion,
422 may be important for BC distribution in the CLP drainage, preliminary BC data from
423 sediment fences and river banks (Boot et al., 2014), along with a report on dissolved and
424 particulate BC export (Wagner et al., 2015) suggests that erosion may be a dominant source
425 of BC loss in this system.

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

437 Forest fire temperatures are difficult to determine and can range from approximately
438 1000 °C in the canopy, a maximum of 850 °C at the surface, averaging approximately 300
439 °C, and rarely exceed 150 °C at 5 cm in the mineral soil (DeBano, 2000; Wolf et al., 2013).
440 While it is tempting to derive HTT of BC deposited on the soil surface following the fire, it
441 must be noted that surface and soil BC is likely a pool integrated across sources pyrolyzed
442 over the range of fire temperatures. The amount of B6CA has been shown to correlate
443 directly with HTT for bark and wood materials, yet no clear relationship exists among
444 B6CA concentrations and temperature of charring for pine needle or leaf derived chars
445 (Schneider et al., 2010; Schneider et al., 2013). Information on HTT from B6CA alone, can
446 be bolstered by also using the ratio of B5CA:B6CA which has a significant inverse linear
447 relationship with combustion temperature. Natural chars range from B5CA:B6CA values
448 1.3 to 1.9 for cooler burning forest fires (~300 °C), 0.8 to 1.4 for hotter grass and shrub
449 fires (~500 °C), and <0.8 for the hottest burning domestic fires (800 °C) (Wolf et al., 2013).
450 In HPF impacted areas, the forest floor had a B5CA:B6CA ratio of 1.2 which would be at the
451 border between grass/shrub and forest fires and yield an integrated predicted temperature
452 of around 400 °C, whereas the B5CA:B6CA ratio for 5-15 cm soils was significantly lower
453 averaging 0.8, corresponding to higher combustion temperature of approximately 600 °C,
454 which matches well with the temperatures that would be predicted from the B6CA content
455 alone. Other studies have suggested that the pattern of BPCAs may be informative for
456 determining the amount of processing by microorganisms (Rodionov et al. 2010), although

457 these correlations have not been empirically validated, and abiotic degradation, such as
458 preferential leaching of less condensed forms of BC, would also shift the relative abundance
459 of the BPCA pattern (Abiven et al., 2011). Thus the greater B6CA content and decreasing
460 B5CA:B6CA ratio in deeper soils from our study may represent either BC derived from
461 greater average HTT in past events, selective removal of less condensed forms of BC
462 through preferential solubilization (Abiven et al., 2011) or other biotic or abiotic
463 degradation of less condensed forms of BC.

464 5. Conclusion

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

482 **Author Contribution**

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

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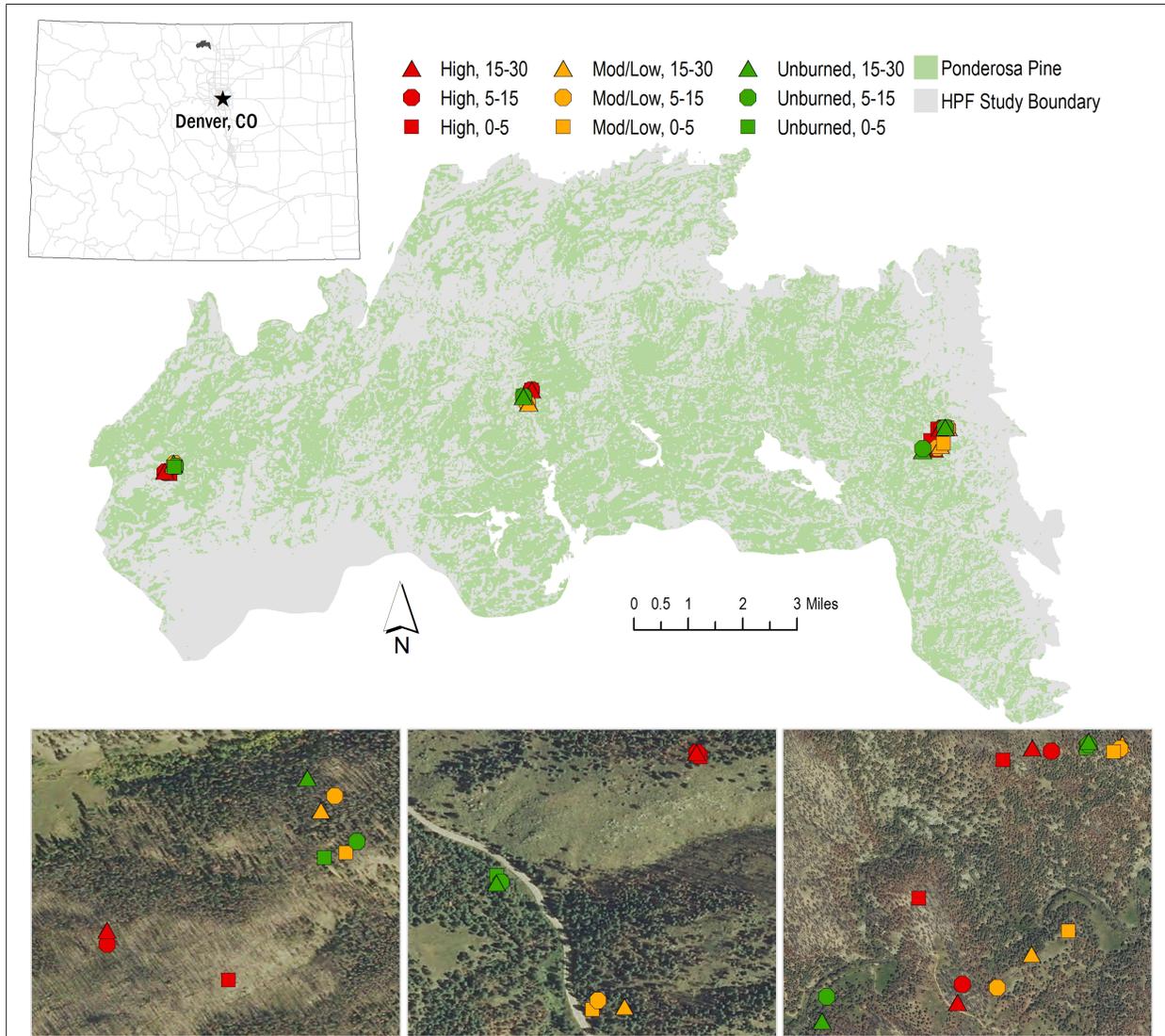
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664

665 **Table 1.** Site characteristics (%C, %N, C:N, C stock) of forest floor, 0-5 cm soils and 5-15
666 cm soil classified by burn severity and slope. Mean values reported with standard errors in
667 parentheses (n=4).
668

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)

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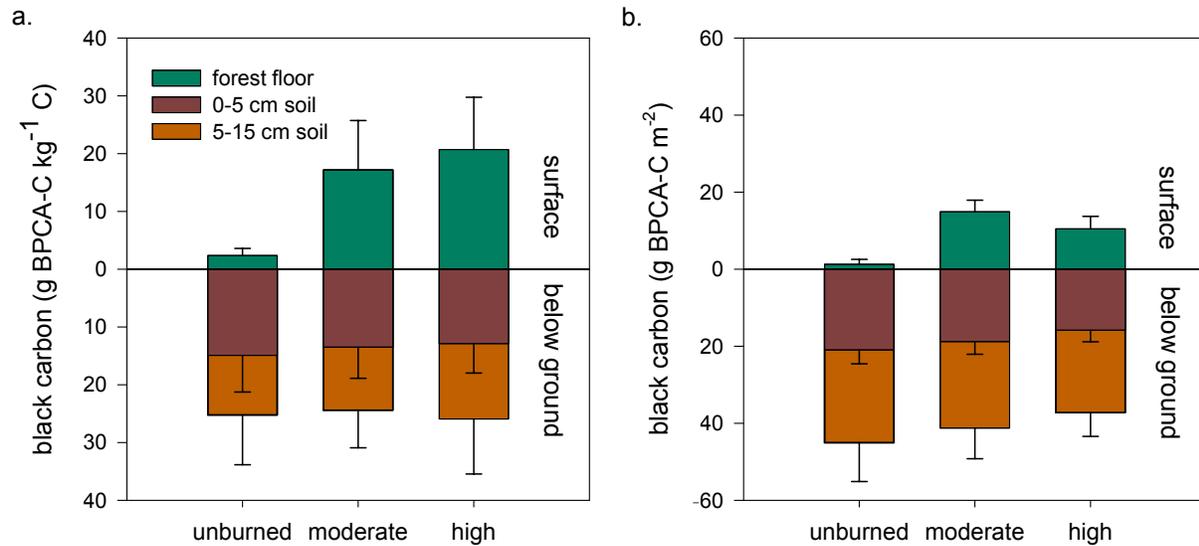


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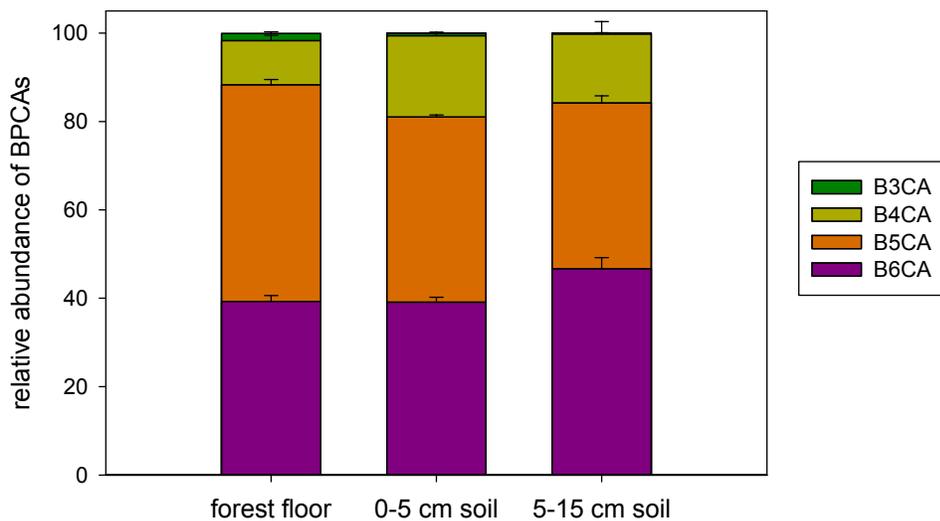
672 Figure 1. Location and classification (burn severity, and slope) of study sites (n=36) in the

673 dominant Ponderosa pine vegetation highlighted in green within the High Park Fire burn

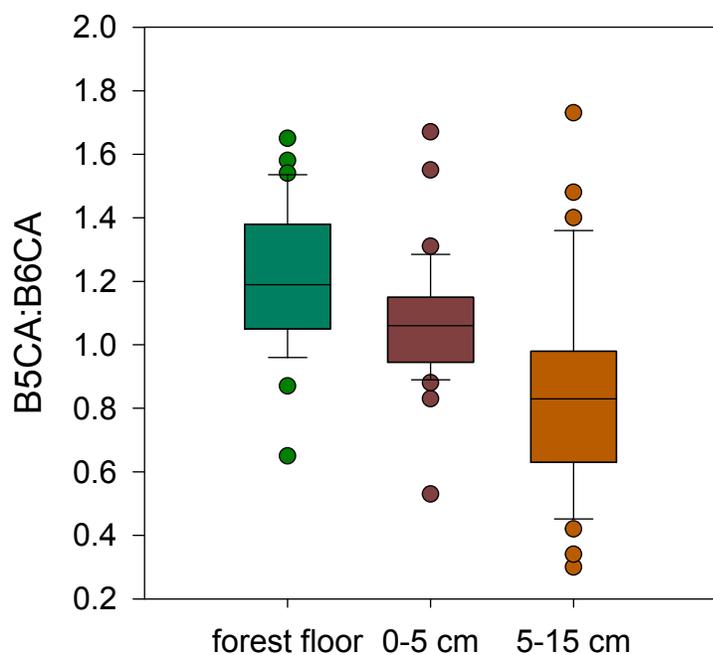
674 area.



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



681
 682 Figure 3. Distribution of BPCAs in each layer (n=36 per layer) illustrating greater relative
 683 abundance of B6CA in 5-15 cm soil versus 0-5 cm soil (p < 0.001) and forest floor
 684 (p<0.001).



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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).