

Article

Long and Short-Term Effects of Fire on Soil Charcoal of a Conifer Forest in Southwest Oregon

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Abstract: In 2002, the Biscuit Wildfire burned a portion of the previously established, replicated conifer unthinned and thinned experimental units of the Siskiyou Long-Term Ecosystem Productivity (LTEP) experiment, southwest Oregon. Charcoal C in pre and post-fire O horizon and mineral soil was quantified by physical separation and a peroxide-acid digestion method. The abrupt, short-term fire event caused O horizon charcoal C to increase by a factor of ten to $>200 \text{ kg C ha}^{-1}$. The thinned wildfire treatment produced less charcoal C than unthinned wildfire and thinned prescribed fire treatments. The charcoal formation rate was 1 to 8% of woody fuels consumed, and this percentage was negatively related to woody fuels consumed, resulting in less charcoal formation with greater fire severity. Charcoal C averaged 2000 kg ha^{-1} in 0–3 cm mineral soil and may have decreased as a result of fire, coincident with convective or erosive loss of mineral soil. Charcoal C in 3–15 cm mineral soil was stable at $5500 \text{ kg C ha}^{-1}$. Long-term soil C sequestration in the Siskiyou LTEP soils is greatly influenced by the contribution of charcoal C, which makes up 20% of mineral soil organic C. This research reiterates the importance of fire to soil C in a southwestern Oregon coniferous forest ecosystem.

Keywords: Biscuit Wildfire; black carbon; charcoal; wildfire; peroxide-acid digestion; pre- and post-fire measurement; soil carbon; soil change

1. Introduction

Wildfires are predicted to become more prevalent and severe in the western United States as climate conditions shift towards warmer and drier fire seasons [1], indicating the need to better understand their impacts. Prescribed fire is often used as a tool for forest restoration; however, these fires rarely reach high temperatures and are not sufficient to be considered proxies for wildfire events [2,3]. Charcoal, a byproduct of wildfires and prescribed fires, incorporated into a forest soil contributes to the long-term carbon (C) sequestration and numerous physical and chemical properties [4–6]. Despite the importance of charcoal on forest soils, there is limited information about the influence of wildfire vs. prescribed fire on soil charcoal.

Soil charcoal is partially combusted organic material from biomass that is incorporated into the O horizon or mineral soil. Charcoal is a constituent of the black carbon continuum, which attempts to explain the range of variability in C of partially combusted vegetative material or fossil fuels [5,6]. It is enriched in C, depleted in nitrogen (N), and highly aromatic in structure [5,6]. This recalcitrant structure makes charcoal highly resistant to physical and biological degradation while the porous, non-polar qualities affect soil physical and chemical properties [4–9]. Previous publications demonstrate increased soil water holding capacity, increased cation exchange capacity, increased pH, and reduced bulk density as a result of charcoal additions into forest mineral soils [4–10].

Charcoal in forest soils can affect C and nutrient storage and cycling. Mean residence time for charcoal can reach over 10,000 years in terrestrial and aquatic sediments, whereas humic acids have a residence time of about 3,000 years [4,5]. Charcoal C composes 10 to 50% of soil organic C [4,11–13]. Charcoal incorporation into forest mineral soils influences N cycling in boreal and temperate forest soils by increasing net nitrification [4,11,14]. Plant available phosphorus also increases under the presence of charcoal [15,16], and charcoal may have similar effects on other soil nutrients although no studies have directly addressed this interaction [16].

Published research quantifying change in charcoal directly with pre- and post-wildfire measurements is absent from current literature. Prescribed fire comparisons are limited to fossil or lake sediment charcoal and rarely use pre-fire charcoal samples from forest soils [17–19]. One prescribed fire study in Florida analyzed pre-fire and post-fire forest floor samples and found increased charcoal concentrations [17]. Charcoal from that study was quantified visually, which may not be suitable for detecting smaller size fractions of charcoal and, therefore, underestimate the actual charcoal content. For wildfires, the chronosequence approach has been used to estimate charcoal dynamics. Changes in charcoal C from wildfires in forest floor and mineral soils were analyzed in Swedish boreal and dry Ponderosa pine forests using chronosequences to represent recent fire history [12,20]. Forest soils in the Swedish forest showed no relationship between soil charcoal content and time since fire [20]. Ponderosa pine forest burned by wildfire 12 years before sampling had nearly twice as much mineral soil charcoal as forest burned 70 years before sampling ($p = 0.09$; [11]). However, the chronosequence

approach assumes the wildfire impact was similar at different sites even though wildfire occurred at different times. It further assumes that pre-fire conditions were the same for sites with different fire histories; not meeting this assumption could confound fire effects with pre-fire spatial differences. Direct measurements of pre- and post-wildfire samples render assumptions concerning pre-fire conditions unnecessary. Studies in which soil C measurements are available before and after wildfires are rare and lack mention of the presence or absence of charcoal [21–24].

The production of charcoal measured by physical determination and consumption of experimentally placed wood in experimental and prescribed fires ranges from 0.4–8.1% of the fuels consumed [17,18,25,26]. Production of charcoal in a Wyoming wildfire was about 8% of coarse woody debris consumed, as estimated from post-fire observations of volumetric conversion of wood to charcoal or visual determination of charcoal on the forest floor [26]. In contrast, estimating wildfire production of charcoal from fine woody debris is even more challenging. Because fine woody debris are largely consumed, post-fire observations cannot be used to estimate pre-fire fine wood fuel loads; instead, pre-fire measurements are needed.

Comparing pre and post-wildfire soil and fuel characteristics is rare because of the unpredictable nature of wildfires. The 2002 Biscuit Wildfire burned a portion of the Siskiyou Long-Term Ecosystem Productivity (LTEP) experiment in the Rogue River—Siskiyou National Forest, OR, [21,22,27]. Pre and post-wildfire soil and fuel sampling at the Siskiyou LTEP site directly quantified how fire-induced losses of soil C and N are related to woody fuels, thinning, fire type, and fire severity [21,22]. Pre and post-wildfire soil sampling of the 2002 Gondola Fire on Lake Tahoe, Nevada, USA quantified wildfire-induced changes in soil C and nutrients [21,22]. However, changes in charcoal C have not been reported for these sites.

The goals of this study are (i) to determine the quantity of soil charcoal C in a southwest Oregon forest; (ii) to determine the change in soil charcoal C as a result of wildfire and prescribed fire; (iii) to quantify the proportion of burned woody fuels that become charcoal. These goals were met by assessment of pre and post-fire soils and woody fuels of the Siskiyou LTEP study [21–23].

2. Results and Discussion

2.1. Charcoal Characterization

In the O horizon, 0.5–4 mm charcoal C is 4 times that of 4–20 mm charcoal C (Table 1). In the mineral soil, <4 mm charcoal C is more than 30 times 4–20 mm charcoal C. Charcoal C concentration decreases from the surface (0–3 cm) to subsurface (3–15 cm) mineral soil (Table 1). Charcoal C is ~6% of total C in the O horizon of burned units, but <1% in unburned units (Table 1). In contrast, charcoal C is ~20% of total C in the mineral soils, irrespective of recent burn history and soil depth.

The contribution of charcoal C to the total carbon in mineral soils is in the middle of the range of published values for studies that used the peroxide-acid method. Charcoal C concentrations reported by Kurth *et al.* [12] range from 14 to 26% of total C in the upper 10 cm of Ponderosa pine forest mineral soils. Boreal Saskatchewan forest soils range from 18 to 22% of total C in the A horizon [28]. Forest soils in the Sierra Nevada Mountains contain charcoal C that represents 10–15% of total C in the upper 6 cm of the mineral soils [13].

Table 1. Charcoal C [mean (standard error, n experimental units)] in soils from Siskiyou-Long-Term Ecosystem Productivity (LTEP) experimental units with recent history of being unburned or burned.

Soil layer		Charcoal C, unburned		Charcoal C, burned	
		mg C g ⁻¹ soil	% of soil C	mg C g ⁻¹ soil	% of soil C
O horizon	0.5–4 mm char particles	1.30 (0.24,3)	0.3	10.7 (2.5,3)	5.3
	4–20 mm char particles	0.37 (0.16,3)	0.1	2.9 (0.7,3)	1.5
Surface	<4 mm soil	13.5 (1.05,2)	17.4	9.7 (0.66,6)	19.6
mineral soil	4–20 mm char particles	0.27 (0.10,2)	0.3	0.30 (0.14,4)	0.6
Subsurface	<4 mm soil	8.4 (0.03,2)	22.8	6.6 (0.3,6)	19.6
mineral soil	4–20 mm char particles	0.04 (0.03,2)	0.1	0.09 (0.03,4)	0.3

Soil texture may explain the variation in charcoal contribution to total C in mineral soils. Higher percentages of silt plus clay correspond to a higher percentage of total C as charcoal C. For example, based on data from a Ponderosa pine forest [11,12,29], our evaluation indicates charcoal C as percentage of total C is positively correlated with silt plus clay concentration. In the boreal transition zone of Saskatchewan, lacustrine soils with 85% silt plus clay have 22% of total C as charcoal C, while fluvial soils consisting of 41% silt plus clay have only 18% of total C as charcoal C [28]. Similarly, Sierra Nevada sandy loams and one silty loam contained 10–15% of total C as charcoal C [13], whereas the Siskiyou-LTEP loam and clay loams had 20% charcoal C. Soil organic C, in general, is stabilized by clay and silt [30–32]. The enhanced percentage of charcoal C with greater silt plus clay suggests charcoal is preferentially stabilized compared with other forms of organic C.

2.2. Pre and Post-Fire Charcoal C

In the burned treatments, charcoal C in the O horizon averaged 35 kg C ha⁻¹ prior to fire and 311 kg C ha⁻¹ one year following fire (Figure 1). The increase in charcoal C was less for the thinned wildfire treatment than for the unthinned wildfire and thinned prescribed fire treatments (Figure 2). For comparison, the charcoal C in the O horizons of a montane Ponderosa pine forest was 10–336 kg C ha⁻¹ [7], and stands exposed to recent multiple fires contained three times more charcoal than stands that had not burned in greater than 79 years [33]. In boreal Swedish forest, somewhat greater values of O horizon charcoal C occur, ranging between 140 and 1620 kg C ha⁻¹ [7,20,34]. However, use of different methods to quantify charcoal C precludes absolute comparisons among the studies. As shown by Hammes *et al.* [35], the various charcoal C quantification methods isolate and measure an array of black C materials along the continuum. The Siskiyou LTEP values are based on physical separation followed by peroxide-oxidation digestion, whereas Ponderosa pine results are from physical separation and the assumption that 80% of charcoal mass is C [4] and boreal Swedish results are from nitric acid and benzenepolycarboxylic acid chemical digestions [20,35].

The charcoal C in the Siskiyou-LTEP mineral soils is the result of long-term, multi-century influences as well as recent disturbance. Charcoal C averaged 2093 (SE ± 107) kg C ha⁻¹ in pre-fire and 1904 (SE ± 101) kg C ha⁻¹ in post-fire surface (0–3 cm) mineral soil. Pre-fire charcoal C averaged 5217 (SE ± 469) kg C ha⁻¹ and post-fire averaged 5317 (SE ± 242) kg C ha⁻¹ in subsurface (3–15 cm) mineral soil (Figure 1). The higher charcoal C masses in the mineral soil compared to O horizons of

the Siskiyou-LTEP study (Figure 1) agree with results from the Ponderosa pine forest, where mineral soil contained 10–30 times more charcoal than O horizon [12,34]. The mineral soils reflect an important pool of charcoal C influenced primarily by the long-term input of charcoal into the forest soils.

Figure 1. Pre and post-fire charcoal C by treatment: unthinned wildfire, thinned wildfire, thinned prescribed fire, unburned. O horizon 0.5–20 mm charcoal fraction. Mineral soil layers < 4 mm charcoal fraction. Mean $\pm$ standard error, $n = 2$.

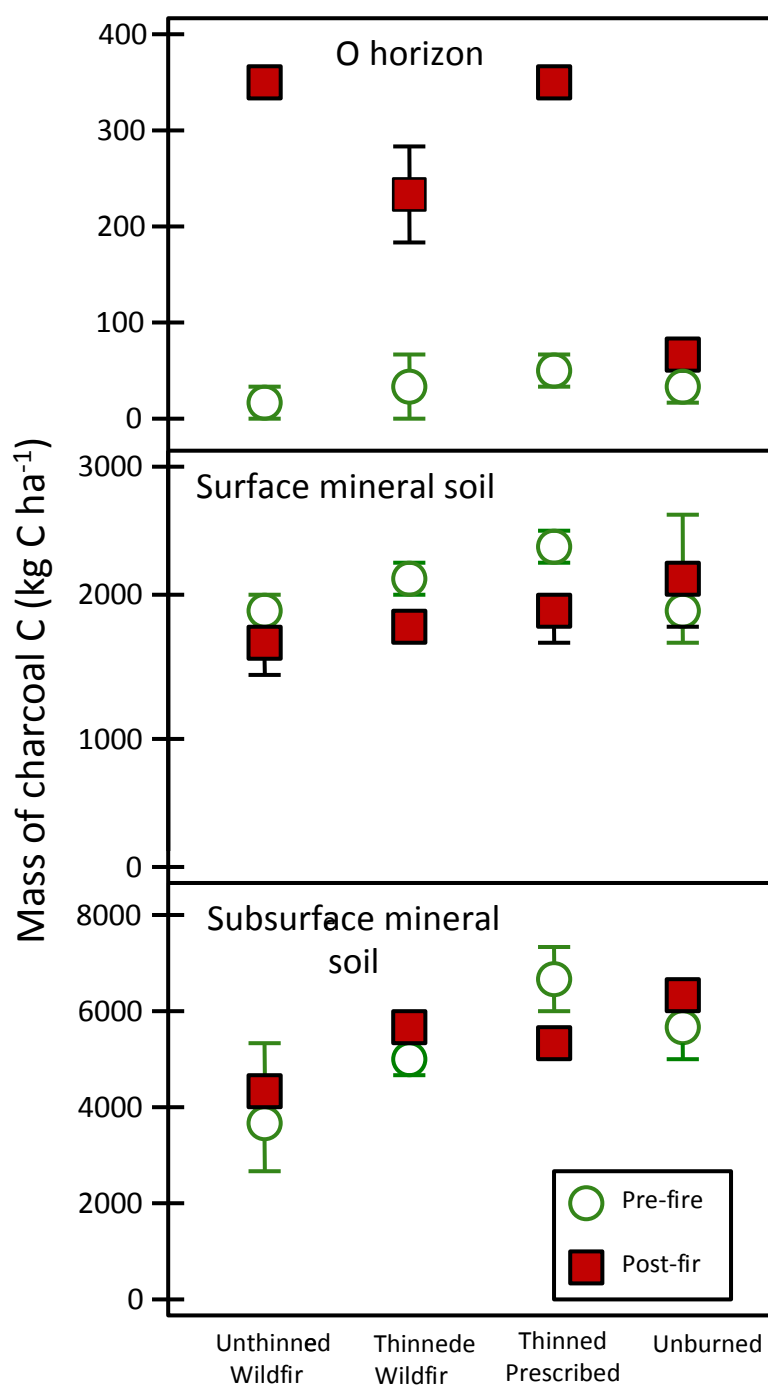
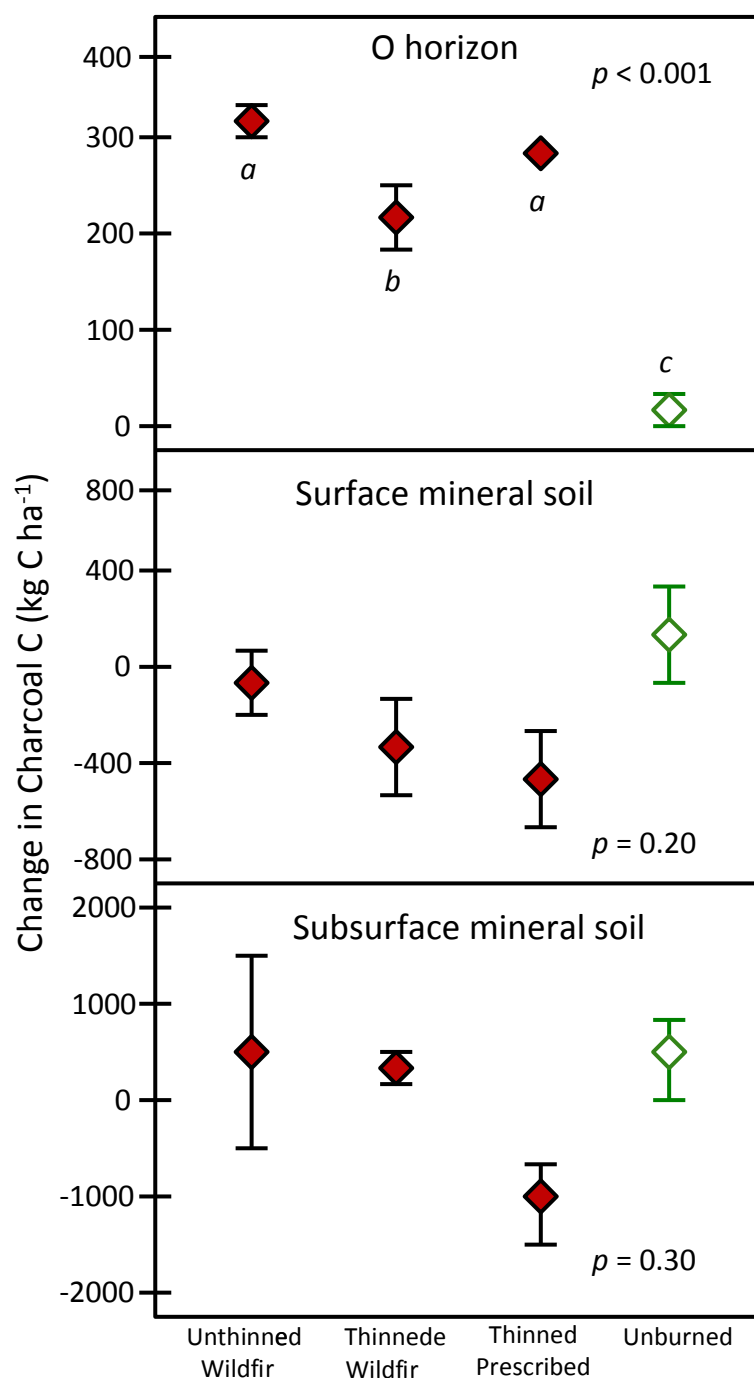


Figure 2. Change in charcoal C mass (mean $\pm$ SE, $n = 2$) for O horizon 0.5–20 mm charcoal and mineral soil < 4 mm fraction. P values are from single factor ANOVA. For O horizon, treatments not identified by the same letter are different, Tukey test, $\alpha = 0.05$.



Comparing the Siskiyou-LTEP soils to published peroxide-acid digestion values from dry Ponderosa pine forest soils [11,12], boreal forest soils [28], and Sierra Nevada forest soils [13], we can identify variables that may influence the long-term charcoal C storage in mineral soils. The contribution of charcoal C to soil C pools may vary with fire history and fire intensity. Under a fire regime with short fire return interval, the frequent fires may completely burn charcoal deposited on the forest floor by previous fires before it can become mixed into the mineral soil. In contrast, infrequent fires may allow time for charcoal incorporation by mixing, as proposed by Brimmer [33] and DeLuca

and Aplet [7]. Also, higher temperature fires have the potential to completely volatilize or convectively transport charcoal particles, leaving less charcoal on the forest floor than a lower temperature fire [7,34]. These processes would lead to a positive relation between mineral soil charcoal and fire return interval. Conversely, in a modeling study of thinned Ponderosa pine, the opposite trend was found, with more mineral soil charcoal resulting from a shorter fire return interval [7].

Comparison of the Siskiyou LTEP site with a dry Ponderosa pine forest supports the positive relationship between fire return interval and charcoal C in mineral soils. In a Ponderosa pine forest, the top 3 cm of mineral soil contains 450–780 kg charcoal C ha⁻¹ and the fire return interval is between 10 and 50 years [11]. The Siskiyou LTEP mineral soil, sampled the summer following the Biscuit Wildfire, has twice as much charcoal C (Figure 1) and more than twice the fire return interval. The site is situated on the west side of the Siskiyou Mountains where the fire return interval ranges from 90 to 150 years [36], which is much longer than further inland [37]. The lower fire return interval in the Ponderosa pine forest may have volatilized charcoal particles deposited from past fire events, leaving less charcoal C accumulation in mineral soils as suggested by DeLuca and Aplet [7].

Evaluation of charcoal in the forests of the Sierra Nevada Mountains [13] supports the positive relation between mineral soil charcoal and fire return interval. In that study, the top 6 cm of mineral soil contained 1000–2100 kg charcoal C ha⁻¹ in an oak woodland site, 2000–4500 kg charcoal C ha⁻¹ in a mixed conifer site, and 3500–4600 kg charcoal C ha⁻¹ in a red fir forest [13]. The fire return interval for the low-elevation woodland site is less than ten years, the mixed conifer site burns every 10 to 20 years, and the red fir site burns at 20 to 30 year intervals [13]. However, the Siskiyou-LTEP results do not extend the positive relation between mineral soil charcoal and fire return interval. The Siskiyou-LTEP charcoal C masses, 2600–3900 kg charcoal C ha⁻¹ for the top 6 cm of mineral soil, are similar to the mixed conifer and red fir sites of the Sierra Nevada soils, even though the Siskiyou fire return interval is much longer at 90–150 years [36].

Bélanger and Pinno [28] reported charcoal C for a boreal forest in Saskatchewan that range from 4000 to 11,000 kg charcoal C ha⁻¹ in the A horizons (depths of 7–13 cm) where the fire return interval is about 75 years or less where agricultural burning occurred, but 15 to 40 year intervals prior to 1890 [28]. Charcoal C masses from the Siskiyou-LTEP soils are almost three times greater than masses for Swedish and Siberian boreal forests, which developed under greater fire return intervals [7,20,34,36]. The Siskiyou-LTEP soils are consistent with the lower range of the boreal values and do not support the idea of a positive relationship between fire return interval and charcoal accumulation. The diverse results of these comparisons suggest that other environmental or inherent soil differences may play a large role in the processes involved in long-term charcoal C storage, such as soil texture, discussed above.

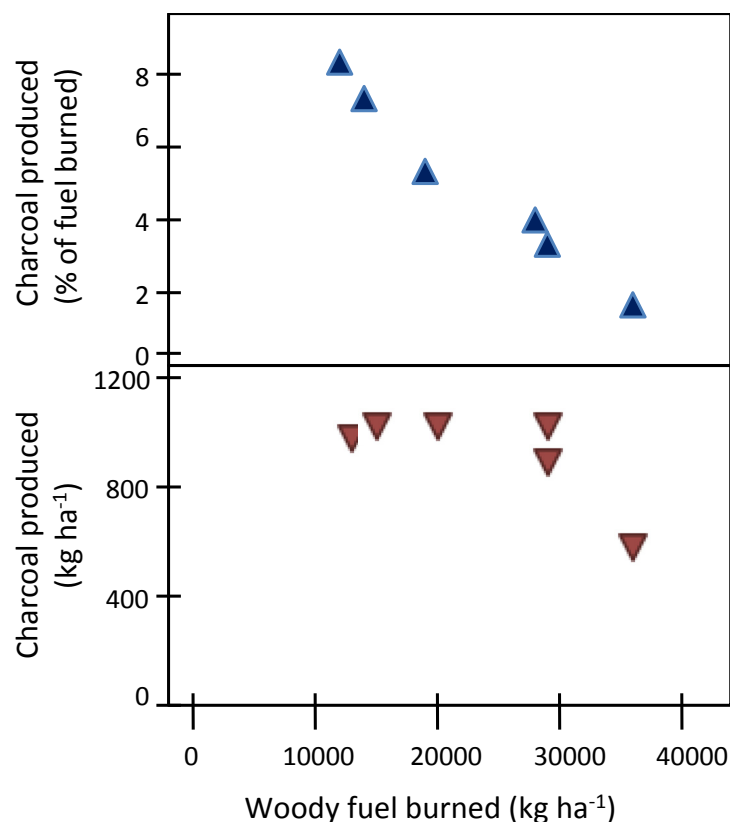
At the Siskiyou LTEP, change in surface mineral soil charcoal C did not differ among burn treatments (Figure 2), but taken together, the burn treatments decreased charcoal C by several hundred kg charcoal C ha⁻¹ compared with the unburned treatment ($p = 0.06$; unburned mean change = 175, SE = 211, $n = 2$; burned mean change = -310, SE = 101, $n = 6$). The loss of charcoal C corresponds to the loss of surface mineral soil via convection erosion during the fire or by post-fire erosion [21]. At the time of sampling, one year post-wildfire, soil may not have been exposed to enough mixing events, leaving the majority of the O horizon charcoal created by the 2002 Biscuit Wildfire remaining on the surface. Accumulation of charcoal in mineral soils is heavily dependent on biological and physical mechanisms that incorporate charcoal into lower soil horizons [7,38]. Other evaluations of recent

wildfire influences on mineral soil charcoal C have used a chronosequence approach, which compares proximal sites that have been exposed to wildfire at different times in the past. These have produced varied results and may confound spatial differences with wildfire effects. For example, at a Ponderosa pine forest, mineral soil charcoal C mass was greater for a 12-year-old burn than 70-year-old burn [11], possibly indicating increase in charcoal by the recent wildfire. But at the same location, mineral soil charcoal C concentrations were similar for 12-year-old and 96-year-old burns [12], providing a different interpretation.

2.3. Charcoal Production and Fuel Consumption

Charcoal production rates ranged from 1 to 8% of woody fuels consumed (Figure 3). The rate was negatively correlated ($r = -0.99$, $p < 0.001$) with amount of woody fuels consumed, resulting in the experimental unit with the greatest fuel loss having the lowest mass of charcoal produced and experiencing the highest fire temperatures, convection, and erosion (Figure 3). This supports the concept that higher fire severity can produce not only a lower percentage of charcoal, but also a lower absolute mass of charcoal. Different percentages of charcoal are produced under different fire conditions. In an experimental field study in Florida forest, prescribed fire moving with the wind produced less than half the charcoal percentage as fire moving against the wind [18]. Fire intensity, oxygen availability and fire duration were cited as possible causes of the difference.

Figure 3. Charcoal produced (top, as % of fuel lost; bottom, as kg ha^{-1}) versus woody fuels lost on six experimental units exposed to wildfire or prescribed fire, Siskiyou Long-term Ecosystem Productivity study, Oregon.



The Siskiyou LTEP charcoal production rates fall within the range observed under a variety of fire and fuel conditions, substrates examined, and measurement approaches. In a prescribed fire in Florida scrub oak forest, pre and post-fire sampling indicated burned stem and leaf biomass yielded 4–6% charcoal from initial mass [17]. In another prescribed fire in Florida, wood experimentally placed on the forest floor produced 0.4–1.5% charcoal [18]. In a lodgepole pine (*Pinus contorta*) forest in a Yellowstone National Park wildfire, Wyoming, USA, post-fire analysis indicated 8% of coarse woody debris consumed by the fire was converted into charcoal [19]. In experimental fires, particle traps indicated 2.2% of the total fuel consumed was converted to charcoal in pine-spruce forest, Northwest Territories, Canada [28], and 2.0% was converted in pine forest, Siberia [38]. The general agreement among charcoal and charcoal C production rates is impressive, given the different techniques used for measurement, sampling and analysis, and their related uncertainties. For example, the Siskiyou LTEP rates do not account for very small (<0.5 mm) or large charcoal (>20 mm).

For assessing C budgets, Forbes *et al.* [39] emphasized distinguishing recalcitrant black C and expressing rates as black C produced as a percentage of total C consumed by fire, rather than charcoal produced as a percentage of biomass burned. Siskiyou LTEP O horizon charcoal particles averaged only 338 g charcoal C kg⁻¹ charcoal, where the charcoal C is defined as resistant to peroxide-acid oxidation. This translates to 1–5 % of total fuel C consumed by fire became charcoal C. This is consistent with Forbes *et al.* [39] summary that <3% of total C consumed in forest fires becomes black C.

The rate of charcoal production is a key consideration in modeling the influence of fire on soil C processes [40]. A number of laboratory and field studies identify the most important factors in assessing charcoal production rates. Fire intensity, fire return interval, vegetation type, fire behavior, and fuel loading represent common factors identified [5,7,13,16,18,38,40]. The Siskiyou-LTEP results provide a clear relation between fuel consumption and charcoal production under wildfire and prescribed fire conditions.

3. Experimental Section

3.1. Study Site

The Siskiyou LTEP site was established on the Rogue River—Siskiyou National Forest in 1992 in relatively homogeneous stands that had naturally regenerated after a wildfire in 1881 [21,40]. The study site is located about 25 km southeast of Gold Beach, OR at an elevation ranging from 750 to 900 m above sea level. Based on 1971 to 2000 values, mean January temperature is 4 °C, mean July temperature is 18 °C, of which only 10 cm falls between June and September [41]. Forest composition is dominated by Douglas-fir (*Pseudotsuga menziesii* var. *menziesii* (Mirb.) Franco) with knobcone pine (*Pinus attenuata* Lemmon) and sugar pine (*Pinus lambertiana* Dougl.). Hardwoods dominate the second story as tanoak (*Lithocarpus densiflorus* (Hook. & Arn.) Rehd.), giant chinquapin (*Chrysolepsis chrysophylla* (Dougl. ex Hook.) Hjelmqvist var. *chrysophylla*), and madrone (*Arbutus menziesii* Pursh.) [21]. Soils are Typic Hapludults and Typic Dystrochrepts developed on a parent material from weathered sandstone and schist-phyllite [21,22,43]. As indicated by Bormann *et al.* [21] the mean C horizon depth is about 35 cm. The total soil inorganic material is comprised of 56% <2 mm,

7% 2–4 mm, and 37% >4 mm, and the <2 mm inorganic material is distributed as 26% clay, 37% silt, and 36% sand [21,22,42].

3.2. Experimental Design

The original experimental design included 27 experimental units that encompassed thinning, clearcutting, and woody debris manipulation in 1997, and prescribed burning in 2001, as described in detail by Bormann *et al.* [21] and Homann *et al.* [22,43]. The Biscuit Wildfire and associated back-burn operation burned 13 of the units in 2002. Of relevance to this study are unthinned and thinned experimental units. The unthinned units were unmanaged and contained 80–110-year-old Douglas-fir (~1000 trees ha⁻¹), some knobcone pine and an understory of tanoak. The thinned units had a relative density averaging 240 trees ha⁻¹; all downed woody material >3 m in length and >5 cm in diameter at the small end was removed, except downed tree tops were retained on units that subsequently underwent prescribed burning. Prescribed burn treatments were fulfilled in the fall of 2001 with light surface fire and no fire reaching into the tree crowns [44]. For this soil charcoal study, two experimental units were evaluated for each of the following categories: unburned, unthinned wildfire, thinned wildfire, and thinned prescribed fire.

The temperatures, conifer mortality, and fire severity rating are displayed in Table 2. Melted aluminum tags denoting sampling points on the experimental units indicated the percentage of area that burned above 700 °C [21]. Conifer mortality was based on pre and post-fire measurements in five 18 by 18 m tree-measurement plots in each experimental unit [21]. BAER burn severity ratings correspond to a measure of soil impact.

Table 2. Siskiyou LTEP experimental units that were evaluated for soil charcoal. The % of area burned at >700 °C and conifer mortality are expanded from Bormann *et al.* [22]. BAER burn severity ratings are from Azuma *et al.* [45]. Minimum mapped BAER polygon was 50 acres whereas treatment areas are 10 to 15 acres [45]. Losses of woody fuels (>1 cm diameter) due to fire are from Homann *et al.* [23].

Fire type	Thinning regime	Unit code	Area burned at >700 °C (%)	Conifer mortality (%)	BAER severity	Woody fuel loss (kg ha ⁻¹)
Unburned	Unthinned	ACC	0	7	n/a	n/a
	Thinned	ATN	0	8	n/a	n/a
Prescribed	Thinned	ATB	0	16	Low	12,500
	Thinned	BTB [†]	33	24	Low	27,900
	Unthinned	BCC	27	86	High	14,400
Wildfire	Unthinned	ICC	63	63	Moderate	19,400
	Thinned	BTN	87	100	High	28,000
	Thinned	IL1	88	97	High	34,800

[†] Unit BTB was within the wildfire perimeter.

3.3. Soil and Charcoal Samples

Soil samples for this study were obtained from the LTEP soil archives, Corvallis, OR. As described by Homann *et al.* [22,43] and Bormann *et al.* [21], soil samples were collected at up to 16 points in each experimental unit before and after fire. Sampling before fire occurred between July and October in 1992 on units ICC and IL1 and in 1995 for the other units. Sampling after the fires occurred in 2003 on all units. Within each experimental unit is a central 2 ha measurement area surrounded by a 4 ha buffer. Measurement areas are further designated by a 25 m by 25 m permanent grid system. Sampling points were proximal to the grid intersections. The measurements from 2003 were ~3 m from 1992 and 1995 points. Where obstructions, usually in the form of trees, rocks, logs, or roots, prohibited sampling access, two additional attempts were made 1 m from the sampling point.

Soil samples were taken perpendicular to the slope, and slope angle was measured. At each point, the O horizon was collected from within a 30 cm diameter ring in 1992 and 1995. After removal of the O horizon, the mineral soil was sampled with a 10 × 15 cm soil corer to a depth of 30 cm. The mineral soil from the corer was extracted and separated into layers. The A horizon was sampled to a varied depth of up to 5.0 cm (average of 3.6 cm), and the B1 horizon was from the bottom of the A horizon to 15 cm. In 2003, similar procedures were used, except the O horizon was collected from within a 21 cm diameter ring and the A horizon was collected to a constant depth of 3 cm from within a 10 × 15 cm frame prior to coring. The separate collection of the A horizon was to prevent the fragile soil structure of the A horizon from being compromised during coring. The O horizon samples were hand-sorted into >4 mm rocks, wood >6.4 mm diameter, >4 mm charcoal, and remaining soil material. One sampling point on an unburned unit was eliminated from analysis because it had >4 mm charcoal from unknown source that was an order of magnitude greater than the other unburned and pre-fire sampling points. Mineral soil samples were sieved into the <4 mm soil fraction and >4 mm fraction, which contained rocks, roots, and large charcoal. Then the fractions were oven-dried at 70 °C and weighed. Slope-corrected soil masses (kg ha⁻¹) were calculated for each horizon. Within each experimental unit, a composite of the soil fraction was made for each horizon. This composite was mass-weighted from the individual sampling points.

Charcoal particles were separated from the O horizon soil composites following methods similar to Brimmer [33]. The O horizon composites were split into subsamples if the entire sample mass was more than 200 g, filtered through a 0.5 mm sieve if <0.5 mm particles were abundant, then spread out on a white tray to be hand separated with the aid of supplemental light. O horizon size fractions less than 0.5 mm were not considered due to the difficulty in visual determination. For 1995 ACC, ATB, and ATN units and 2003 C, BTB, and BTN units, the charcoal was separated into <4 mm and 4–20 mm fractions. For 2003 ACC, ATB, ATN, BCC, BTB, and BTN units, 4–20 mm charcoal particles were hand-separated from A and B1 horizons from individual sampling points. Charcoal particles >20 mm in size were rare and were not quantified in this study.

3.4. Charcoal Quantification and Analysis

Charcoal C was measured in the following samples: surface (A) and subsurface (B1) soil horizon composites, 0.5–20 mm charcoal particles from selected O horizon samples, and charcoal and soils

from the black C reference materials established by Hammes *et al.* [35]. Charcoal C was quantified by the method of Kurth *et al.* [12]. Charcoal and soils were dried for 24 hr at 60 °C and then exposed to the peroxide-acid digestion, as follows. One gram of mineral soil sample or 0.5 g charcoal was ground to a fine powder with a ball mill and placed into a 125 ml Erlenmeyer flask in which 20 ml of 30% H₂O₂ and 10 ml of 1 M HNO₃ were added and occasionally swirled at room temperature over a 30 min period. The flask was then heated in a water bath to 90 °C for 16 hours. After digestion, the suspensions were filtered through Whatman #2 filter papers (Whatman Ltd., Lawrence, KS, USA); filter papers were dried at 60 °C for 24 hours and weighed. Papers had been weighed prior to filtration and mass of residual material was determined as the difference in mass before and after filtration. Residual material was ground with mortar and pestle. Digestions were replicated on two different days.

Total C concentrations prior to and after digestion were determined on a Thermo NC 1112 Analyzer (CE Elantech, Inc., Lakewood, NJ, USA). Siskiyou-LTEP soils were measured against standard curves created with atropine (70.6% C). Total C of the charcoals and soils before digestions were assumed to represent organic C; Siskiyou soil pH is <5, indicating no or limited inorganic C. Total C after digestion is reported as charcoal C and assumes that all non-charcoal organic C is consumed during the peroxide-acid digestion. Duplicate measurements of charcoal C had an average coefficient-of-variation of 17%.

To allow future cross-referencing with other studies, black C reference chars and soils were acquired and exposed to the peroxide-acid digestion method [35,46,47]. The chars had been formed from grass straw (*Oryza sativa*) and chestnut wood (*Castanea sativa*) that had been collected in southern Switzerland. The chestnut wood was debarked and grass bundled then charred at 450 °C for 5 hours and ground when cooled. The H/C, O/C ratios, organic carbon content, and other chemical and physical characteristics of the chars are reported in Hammes *et al.* [46,47]. The Australian Vertisol is a sandy clay soil sampled at 0–10 cm depth at Urrbrae, South Australia, containing 37% clay [35]. The German Chernozem soil is a light sandy clay sampled at 20–60 cm depth in the Hildesheim-Braunschweig region, Harsum, Germany, and consists of 19% clay [35]. Our peroxide-acid charcoal C concentration, as % of organic C, was 9.1% for the Chernozem, 17.0% for the Vertisol, 19.0% for grass char, and no charcoal C was measured for the wood char.

3.5. Data Analysis

Charcoal C concentrations of mineral soil samples and charcoal particles were determined with the following calculation:

$$\text{Charcoal C} \left(\frac{\text{g charcoal C}}{\text{kg sample}} \right) = C_{\text{digested}} \left(\frac{\text{g C}}{\text{kg digested}} \right) \times M_{\text{digested}} \left(\frac{\text{kg digested}}{\text{kg sample}} \right) \quad (1)$$

where C_{digested} is the C concentration in the digested sample and M_{digested} is the mass of the digested sample relative to the undigested sample.

Charcoal C concentrations for O horizon soils were calculated with the following formula:

$$\text{Charcoal C} \left(\frac{\text{g charcoal C}}{\text{kg O horizon}} \right) = C_{\text{particle}} \left(\frac{\text{g charcoal C}}{\text{kg particle}} \right) \times M_{\text{particle}} \left(\frac{\text{kg particle}}{\text{kg O horizon}} \right) \quad (2)$$

where C_{particle} is the concentration of charcoal C in charcoal particles from Equation (1); and M_{particle} is the mass of charcoal particles in the O horizon; C_{particle} was measured on a subset of samples (mean 338 g charcoal C ha^{-1} , $\text{SE} \pm 51$, $n = 2$) and applied to all O horizons.

O horizon charcoal C mass (kg C ha^{-1}) was calculated by multiplying charcoal C concentration by O horizon soil areal mass. Mineral soil charcoal C mass for post-fire samples was calculated by multiplying charcoal C concentration by <4-mm soil areal mass for each of the surface (0–3 cm) and subsurface (3–15 cm) layers. To compare post-fire mineral soil C mass with pre-fire values, pre-fire mineral soil C mass for each layer was determined by the comparable layer approach, which accounts for bulk density changes and mineral-soil loss resulting from fire, as detailed in Bormann *et al.* [21] and Homann *et al.* [22].

3.6. Statistical Analysis

The Biscuit Wildfire disrupted the original LTEP experimental design, but replicated experimental units ($n = 2$ for each of the four treatments: unthinned wildfire, thinned wildfire, thinned prescribed fire, and unburned) allow examining the change in charcoal C mass from before to after fire. For each of the O horizon, surface (0–3 cm) mineral soil, and subsurface (3–15 cm) mineral soil layers, a single factor ANOVA followed by Tukey's multiple comparison test was used to compare among the four treatments [48]. Pearson correlation was used to examine the relation between charcoal production and woody fuels consumed.

4. Conclusions

The burning of a portion of the conifer forest at the Siskiyou-LTEP experiment by the 2002 Biscuit Wildfire provided unprecedented opportunity to directly measure the fire effects on soils across different forest structures. Soil properties and fuel loading were measured prior to the wildfire, which allowed for comparisons of forest treatments under wildfire conditions that are unique in current literature.

Long-term soil C sequestration in the Siskiyou-LTEP soils is greatly influenced by the contribution of charcoal C, which comprises 20% of the total C pool in the surface and subsurface mineral soils. Comparison with other studies indicates this percentage is positively correlated with silt plus clay. In the short-term, charcoal C in the O horizon was greatly increased by burning, with thinned wildfire treatment producing less charcoal C than unthinned wildfire and thinned prescribed fire treatments. A negative relation between percentage of charcoal formed and woody fuels consumed demonstrates an important linkage for forecasting soil responses under different fuel regimes. The newly formed O-horizon charcoal serves as a potential future source to replenish mineral soil charcoal C, which may have decreased during or after fire as a result of combustion, convection and erosion.

The conifer forest of the Siskiyou LTEP shows ample evidence of long-term charcoal C storage in the mineral soil, as well as short-term charcoal C changes in the O horizons due to the Biscuit Wildfire of 2002. Natural fire regimes have resulted in an incorporation of charcoal into the Siskiyou-LTEP soils, without which belowground C storage, and possibly soil chemistry and nutrient composition, would be substantially altered.

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Conflict of Interest

The authors declare no conflict of interest.

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