

Article

Charcoal and Total Carbon in Soils from Foothills Shrublands to Subalpine Forests in the Colorado Front Range

Christopher Licata ^{1,*} and Robert Sanford ²

- ¹ Department of Biological Sciences, University of Denver, 2190 East Iliff Ave., Denver, CO 80208, USA
- ² School of Earth Sciences & Environmental Sustainability, University of Northern Arizona,
 P.O. Box 4099, Flagstaff, AZ 86011, USA; E-Mail: Robert.Sanford@nau.edu
- * Author to whom correspondence should be addressed; E-Mail: pioneer.licata@gmail.com; Tel.: +1-303-465-3181; Fax: +1-303-465-3181.

Received: 2 August 2012; in revised form: 11 October 2012 / Accepted: 15 October 2012 / Published: 22 October 2012

Abstract: Temperate conifer forests in the Colorado Front Range are fire-adapted ecosystems where wildland fires leave a legacy in the form of char and charcoal. Long-term soil charcoal C (CC) pools result from the combined effects of wildland fires, aboveground biomass characteristics and soil transfer mechanisms. We measured CC pools in surface soils (0–10 cm) at mid-slope positions on east facing aspects in five continuous foothills shrubland and conifer forest types. We found a significant statistical effect of vegetation type on CC pools along this ecological gradient, but not a linear pattern increasing with elevation gain. There is a weak bimodal pattern of CC gain with elevation between foothills shrublands (1.2 mg CC ha⁻¹) and the lower montane, ponderosa pine (1.5 mg CC ha⁻¹) and Douglas-fir (1.5 mg CC ha⁻¹) forest types prior to a mid-elevation decline in upper montane lodgepole pine forests (1.2 mg CC ha⁻¹) before increasing again in the spruce/subalpine fir forests (1.5 mg CC ha⁻¹). We propose that CC forms and accumulates via unique ecological conditions such as fire regime. The range of soil CC amounts and ratios of CC to total SOC are comparable to but lower than other regional estimates.

Keywords: charcoal; black carbon; fire; forests; soil organic carbon; Rocky Mountains; fire regime

1. Introduction

Temperate conifer forests and foothills shrublands in the Colorado Front Range of the Rocky Mountains are fire-adapted ecosystems where wildland fires leave a legacy of black C (BC) on the landscape. Black C is a generalized term applied to thermally-altered vegetation. Low burn temperatures produce visible char and charcoal (>0.4 mm dia.) [1] while high burn temperatures yield fine material referred to as pyrogenic C and soot [2]. Here, the term charcoal C (CC) is used to define the BC fraction that is resistant to a weak nitric acid (HNO₃)/hydrogen peroxide (H₂O₂) digest. Charcoal accumulates in soils through various transfer mechanisms and is retained potentially from centuries to millennia [3]. Fire-derived charcoal is an integrated component in temperate conifer forest soils, linked to increased total soil organic C (SOC) pools [4] and inorganic nitrogen (N) availability [5,6].

During wildland fires, BC products are generated from the incomplete combustion of non-woody and woody vegetation. The source material and initial conditions influence subsequent physical and chemical properties [7]. Total cellulose or lignin content determines whether char or charcoal is produced [8]. Cellulose-based char is derived primarily from grasses, forest floor duff and small coarse woody debris (CWD). Charcoal is formed from large CWD and scorched tree stems with high lignin content during post-frontal smoldering and glowing combustion processes, rather than the initial flaming front of a fire [8]. The total quantity and properties of fire-derived charcoal produced during a single fire are linked to both fire behavior and aboveground biomass type and availability [9]. For temperate conifer forests, Tinker and Knight [10] provide a published conversion constant of CWD to charcoal. They estimated that 8% of available pre-burn biomass for large CWD (\geq 7.6 cm diameter) was converted to CC assuming an 85% C content.

Soil mixing causes surface charcoal deposits to move downward in a soil profile and reduces losses from physical transport mechanisms and exposure to repeated fires. Surface to soil charcoal mixing rates and mechanisms vary across ecosystems as a function of bio-activity and abiotic processes [11]. In cold boreal forests, charcoal is retained on the forest floor and in the immediate surface soil horizons [12], whereas in temperate conifer forests, most charcoal is stored primarily in the upper mineral horizons where there is less fire exposure [13]. Mixing rates in fire-adapted conifer forests are unknown and will need to be addressed in future research.

Repeated burns over decades and centuries result in unique fire regimes that are based on fire frequency, fire severity, fuel characteristics and fuel consumption patterns [14,15]. Previous studies [16–18] provide overviews of how regional climatic patterns interact with spatial fuel characteristics to drive fire behavior in the Rocky Mountains. A fire regime classification system for the Colorado Front Range has been classified in three categories; (1) frequent, low-severity (0–35 years), (2) frequent and infrequent, mixed-severity (35–200 years) and (3) infrequent, high severity (>200 years) [19]. Here we use fire regime as one of the criteria used to explain soil charcoal C mass in four montane forests and one foothills shrubland along an elevation gradient from lower to upper treeline.

Soil CC pools develop from the combined effects of repeated wildland fires, aboveground biomass productivity that occurs between fires and soil cycling processes. These effects are best summarized as the five phases of charcoal pool development: (1) aboveground biomass growth, (2) biomass loss and

charcoal formation during a fire, (3) charcoal to soil flux, (4) soil charcoal degradation and loss, and (5) long-term retention. There have been few studies that have quantified CC in Rocky Mountain soils [9,20]. This research is focused on the retention phase by quantifying surface soil (0–10 cm) CC mass. Our additional objectives are to evaluate the mechanisms that cause BC formation and retention in the dominant Colorado Front Range vegetation types. These data provide baseline information that may be integrated into ecosystem C cycle models and applied research to evaluate ecological or biological responses to charcoal additions.

Ecological conditions based on differences in aboveground biomass, fire behavior and soil properties are expected to influence fuel consumption patterns, CC and SOC formation and subsequent soil accumulation/retention rates. Vegetation types with comparatively higher surface fuels and cooler conditions with less frequent fires are expected to contain more surface charcoal. This is based on the assumption that more fuel, less bio-activity and infrequent fires allows charcoal to accumulate. Under this premise, we expect charcoal pools to increase with elevation along this ecological gradient. Therefore, we hypothesize that fire-derived CC in the upper 10 cm of mineral soil will vary by vegetation type. We also test the hypothesis that SOC varies across these same vegetation types. This study yielded the largest collection of soil samples analyzed for CC in the United States.

2. Materials and Methods

2.1. Experimental Design and Field Sampling

Forest distribution in the Colorado Front Range is influenced by combinations of topographic and moisture gradients [21]. The general pattern is foothill shrublands dominated by mountain mahogany (*Cercocarpus montanus*) at the lowest elevations which transitions to open montane forests dominated by ponderosa pine (*Pinus ponderosa var. scopulorum*) on warm, dry sites and Rocky Mountain Douglas-fir (*Pseudotsuga menziesii subsp. glauca*) on cool, moist sites. At mid-elevations, closed montane forests of Rocky Mountain lodgepole pine (*Pinus contorta var. latifolia*) is often dominant or co-dominant with other conifers and aspen (*Populus tremuloides*). Subalpine forests grow at high elevations with Engelmann spruce (*Picea engelmannii*) and subalpine fir (*Abies lasiocarpa*) co-dominant throughout.

Birkeland *et al.* [22] conducted soil profile analyses along elevation and slope transects throughout the Colorado Front Range. Low elevation soils are mostly Cryolls with deep, dark surface mineral horizons (A horizon) in comparison to uppermost elevations; this is due to high soil organic matter content and a less developed zone of Fe^{3+} and Al^{3+} leaching (E horizon). At mid-elevations, montane soils are classified as Cryolls on warmer slopes and Cryalfs in colder areas. Soils above approximately 2700 m are Cryepts which are cold, young soils. In these soils, there is little or no clay formation and accumulation with chronic acidic conditions in the A horizons. Most of the area above 2700 m was also covered by the Pinedale glacial event. Soils, vegetation type and fire regime are used together to help explain the results of this study in the context of the Colorado Front range (see below).

Soil samples were collected in the Bear Creek and Clear Creek watersheds, located west of Denver, CO (Figure 1). All of the major fire regimes and vegetation types from the region are present in the study area. The western portion of the study area is mostly in the Mount Evans Wilderness Area on the Arapaho and Pike National Forests with the east portion largely private property with isolated public

land units. Field observation, prior research on forest distribution [21] and current, GIS-based existing vegetation type maps [23] all aided in identifying the five vegetation types and associated 200 m elevation sampling bands (Figure 1).

Figure 1. Location of the soil charcoal sampling area with current vegetation types west of Denver, CO in the Colorado Front Range. Geospatial data was acquired from United States Geological Service (USGS) GAP Analysis Project [23] and United States Farm Services Agency (FSA) National Agricultural Imagery Program [24].



In order to test the main effect of vegetation type on CC and soil organic C pools, we reduced landscape variation with a stratified random plot design. A digital elevation model (DEM) of the study area was used to identify 200 m elevation bands that were centered midway between the upper and lower limits of each vegetation type. Subsequently, sites on east-facing aspects ($67^{\circ}-112^{\circ}$ azimuth) with slopes 5%–30% were combined with the vegetation layer to create sets of potential sample polygons within all five of the centered elevation bands (North American Datum 1983, UTM Zone 13 North). ArcMap 9.3 and the embedded spatial analyst extension were used to identify potential sampling polygons and select random plot locations, all within 2 km of existing roads (to make access feasible). Within the stratified random set of polygons, 10 plot centers were assigned a 0.25 ha (25 m × 25 m) square in each of the vegetation types. In the summers 2009 and 2010 mineral soils were sampled in each of the 0.25 ha plots with 10 random sample points spaced a minimum of 3 m apart to

avoid overlap. Three composite soil cores were collected at each sample point using a round metal probe (2.5 cm diameter) where the litter layer was moved and only the upper 10 cm of mineral soil collected. This depth was selected to allow consistent comparison across the vegetation types.

Both SOC and CC data were converted from concentration (g kg⁻¹) to mass (mg ha⁻¹) using field-derived bulk density (BD) measurements. Bulk density was sampled at a sub-set of 3 sample points per vegetation type with a double-cylinder probe (3 cm diameter \times 5 cm length) pounded vertically into the soil. Bulk density was higher for the low elevation vegetation types (1.16 and 1.31 g cm⁻³) where there are primarily coarse-textured soils. In comparison, higher elevation lodgepole pine and spruce/subalpine fir had lower BD (1.01 and 1.09 g cm⁻³) due to finer-textured soils and residual glacial material.

2.2. Laboratory Methods

Soil samples were analyzed for CC with a modified version of the Kurth-Mackenzie-DeLuca (KMD) method [4,20]. The KMD method couples total CHN analysis via dry combustion with a thermo-chemical digestion that uses heating and a weak nitric acid/hydrogen peroxide solution to degrade labile soil organic matter and low-temperature char while retaining more resistant charcoal. Kurth *et al.* [20] summarized a method comparison test and demonstrated that the KMD method is effective in estimating soil charcoal content in spiked samples ranging from 0.5% to 5.0% (wet weight). We modified this method by substituting hotplates and 250 mL flasks with a Technicon BD-46 aluminum block heater with 75 mL round-bottom glass tubes with reflux chambers and glass inserts. Block digests allowed for accurate temperature control and increased the efficiency of sample runs.

Each soil sample was oven-dried at 60 °C for 48 h, sieved to 2.0 mm and pulverized in a ball grinder for 1 min. A subsample was put aside to determine SOC. For the digest, 1.0 g of oven-dry soil was added to the glass tubes along with 10 mL of 1 M HNO₃ (nitric acid) and 20 mL of 35% H₂O₂ (technical grade hydrogen peroxide). Tubes were swirled and then placed in the block and left unheated for 30 min. To contain the vigorous reaction, temperatures were ramped to 50 °C for 30 min and 70 °C for 30 min before being heated to 100 °C for 16 h. Following the digest, samples were cooled, swirled and filtered through plastic funnels lined with Whatman #2 filter paper into scintillation vials. The liquid in the vials was discarded leaving only fine soil material which was oven dried for 24 h at 60 °C. In preparation for total C analysis, the dried soil was re-homogenized with a mortar and pestle.

For both SOC and post-digest samples, a Carlo-Erba 1108-CHNS was used to measure total C. Approximately 15.0 mg of soil was placed into a tin capsule (5×9 mm) and consumed at 1000 °C. An internal lab standard was developed from a local soil collected from deep horizon material with very low total C and CC present. This allowed tracking of run to run variation and estimation of the method sensitivity under very low C concentrations (results not presented).

2.3. Statistical Analysis

A nested, general linear mixed model (GLMM), which allows both fixed and random effects in the model design, was used for testing the mean SOC, CC amounts and CC/SOC ratios between

vegetation types ($\alpha = 0.05$). The advantage of a GLMM compared to a general linear model analysis of variance (GLM ANOVA) is that the total error in the model is divided between the fixed and random factors reducing Type II errors [25]. A nested approach was used based on the suggestions in Wampold and Serlin [26] that nesting appropriate model factors avoids an invalidation of the test hypothesis. Vegetation type is assumed to be a fixed, categorical variable due to the distinct sampling elevation bands. Soil organic C and CC were analyzed as either the dependent variable or as a random, continuous co-variate in two separate model runs. Additional random model effects were the two nested factors: 1) individual samples nested within plot and vegetation type and 2) plots nested within vegetation type. Least squares post hoc procedures (Tukey-Kramer adjustment) were applied to test for significant pairwise differences. All statistical analyses were performed with restricted maximum likelihood estimation and the Kenwald-Roger degrees of freedom method in PROC MIXED (SAS 9.2 with Enterprise 4.2 Interface).

3. Results

The main effects of vegetation type on soil CC are significant ($F_{5,52.8} = 12.4$, p < 0.0001) and soil organic C ($F_{5,49.9} = 24.6$, p < 0.0001) (Table 1). Least squares, post-hoc procedures identified significant mean pairwise differences for SOC between ponderosa pine and lodgepole pine and Douglas-fir. However, these same procedures in the charcoal C post-hoc analysis did not identify significant differences (Figure 2). Therefore we accept the general hypothesis that SOC and CC vary by vegetation type, but we can make specific vegetation type comparisons for SOC only. Co-variance parameter tests demonstrated that when SOC (Pr > Z = 0.24) or CC (Pr > Z = 0.24) were entered into the model as a random, continuous co-variate, they did not have a significant effect on the dependent variable. In spite of this finding, these variables were retained in the final model to ensure proper model error distribution. The CC/SOC ratios were significantly different between vegetation types ($F_{5,45.1} = 111.04$, p < 0.0001). Post-hoc analysis identified significant pairwise differences between lodgepole pine and foothills shrublands.

There is a weak bimodal distribution trend across this landscape with the lowest charcoal C in the foothills shrublands (1.2 mg CC ha⁻¹) followed by higher CC in ponderosa pine (1.5 mg CC ha⁻¹) and Douglas-fir (1.5 mg CC ha⁻¹) but then decreasing in lodgepole pine (1.2 mg CC ha⁻¹) before increasing again in spruce/subalpine fir (1.5 mg CC ha⁻¹). Soil organic C follows a similar pattern with the exception being a decline between ponderosa pine (30.5 mg CC ha⁻¹) and Douglas-fir (18.8 mg CC ha⁻¹). Ponderosa pine had the most SOC followed by spruce/subalpine fir (23.7 mg C ha⁻¹), foothills shrublands (22.1 mg C ha⁻¹), Douglas-fir and then lodgepole pine (15.2 mg C ha⁻¹) with approximately 50% less total C than ponderosa pine. The CC/SOC ratios by vegetation type are highest in lodgepole pine and Douglas-fir (0.08) and lowest in foothills shrublands (0.05) with intermediate ratios for spruce/subalpine fir (0.07) and ponderosa pine (0.06).

Table 1. Soil organic C (SOC), charcoal C (CC) and bulk density (BD) in upper 10 cm mineral soil for five vegetation types along an ecological gradient in the Colorado Front Range with +/-1 standard error in parentheses (n = 10) and the CC/SOC ratio.

Vegetation Type (sampling elevation)	SOC (g kg ⁻¹)	CC (g kg ⁻¹)	BD ^a (g cm ⁻³)	SOC (mg ha ⁻¹)	CC (mg ha ⁻¹)	CC/SOC ^b
Foothills shrublands (1700–1900 m)	19.1 (0.8)	1.1 (0.1)	1.16	22.1 (1.0)	1.2 (0.1)	0.05 ^ª
Ponderosa pine (1900–2100 m)	23.3 (1.4)	1.1 (0.1)	1.31	30.5 (1.9)	1.5 (0.1)	0.06 ^{ab}
Douglas-fir (2400–2600 m)	14.6 (0.8)	1.1 (0.1)	1.29	18.8 (1.0)	1.5 (0.1)	0.08 ^{ab}
Lodgepole pine (2800–3000 m)	15.0 (0.8)	1.2 (0.1)	1.01	15.2 (0.8)	1.2 (0.1)	0.08 ^b
Spruce/subalpine fir (3200–3400 m)	21.8 (1.1)	1.4 (0.1)	1.09	23.7 (1.2)	1.5 (0.1)	0.07^{ab}

^a: Bulk Density, n = 3; ^b: Mixed-model type 3 tests show that CC/SOC ratios are significantly different between vegetation types ($F_{5,45,1} = 111.04$, p < 0.0001). Different lower case letters denote significant pairwise comparisons following Tukey-Kramer post-hoc analysis ($\alpha = 0.05$).

Figure 2. (1) Soil organic C and (2) charcoal C in upper 10 cm mineral soil for five vegetation types along an elevation transect in the Colorado Front Range. Bars are one standard error about the mean (n = 10). Mixed-model type 3 tests found significant main effects of vegetation type on 1) soil organic C ($F_{5,49.9} = 24.6$, p < 0.0001) and 2) charcoal C ($F_{5,52.8} = 12.4$, p < 0.0001). Different lower case letters denote significant pairwise differences from Tukey-Kramer post-hoc analysis ($\alpha = 0.05$). Degrees of freedom were calculated with Kenwald-Roger method in PROC MIXED (SAS 9.2 and Enterprise Guide 4.2).



4. Discussion

Overall, soil charcoal pools reported here are comparable to results from other temperate forest and shrubland ecosystems [4,27]. We identified a significant main effect (GLMM analysis) of vegetation type on SOC and CC content from foothill shrublands to subalpine forests along the Colorado Front Range. Unique to this study, we found that SOC and CC in surface mineral soil pools do not increase with elevation gain but instead there is a weak bimodal pattern across this landscape. These results support the observation that total SOC pools and fire-derived charcoal form and accumulate via fire regime and soil properties which are related to vegetation type.

Differences in ecological conditions in the study area are applied here to interpret the overall patterns of soil charcoal (Table 2). From an aboveground perspective, the most important influences on soil CC pools are fire regime and available biomass sources. For example, foothills shrublands (1700–1900 m) and lodgepole pine forests (2800–3000 m) occur at different elevations but have similar mean CC amounts, which are also the lowest among all vegetation types. For foothills shrublands, it is the combination of high surface fire frequency and low lignin-based fuel sources that result in less charcoal formed per fire. This is an outcome of the limited time for re-growth but more burns to contribute charcoal over time. In temperate grassland ecosystems with repeated surface fires, BC can complex with existing soil organic matter leading to long-term retention [28,29]. Foothills shrublands have ubiquitous grass cover and are likely to retain soil charcoal in a similar manner. Finally, this may be an under-estimation of shrubland CC given charcoal movement to deeper layers in the profile [30].

Conversely, lodgepole pine forests include moderate amounts of lignin-based surface fuels with an infrequent fire regime [31]. In this forest type, replacement-severity fires are more likely to burn through the forest canopy more than the forest floor, producing moderate amounts of charcoal on standing trees (*i.e.* vertical fuels) that fall to the forest floor in a delayed contribution phase [5]. For these forests, low soil CC amounts may be attributed to reduced contributions from vertical fuels, relatively more forest floor surface storage and sparse understory vegetation.

The difference between these two vegetation types is also reflected in the CC/SOC ratios. These ratios demonstrate how much charcoal retention there is relative to the total SOC pool. Foothills shrublands had the lowest CC/SOC ratio based on low CC and a moderate SOC pool. In these soils, warm soil conditions and the frequent fire return interval combine resulting in a large SOC pool with low CC. A closed tree canopy, less fire frequency and colder soil conditions in lodgepole pine forests lead to a relatively smaller SOC pool but similar amounts of CC and a significantly higher CC/SOC ratio.

It is vegetation type that gives insight into comparably higher CC in spruce/subalpine fir, ponderosa pine and Douglas-fir forests. Spruce/subalpine fir forests have the coldest climate, the slowest ecosystem decomposition rates and longest fire return interval of all the vegetation types. Very infrequent fires allow lignin-based surface fuels and a deep duff layer (cellulose-based) to accumulate. The combination of two large BC sources as well as replacement-severity fires result in relatively higher CC per fire. There are comparable amounts of soil charcoal compared to the ponderosa pine and Douglas-fir forests in spite of reduced bio-activity and thus soil mixing. This finding suggests that surface charcoal is transferred into the soil via a separate soil-related process in colder forest types.

Forests 2012, 3

Table 2. Generalized charcoal sources, fire regimes and soil processes that influence soil charcoal carbon (CC) pools across five vegetation types along an ecological gradient in the Colorado Front Range.

Vegetation Type	CC Source ^a	Fire Regime ^b	Soil Process ^c
Foothills shrublands	moderate to high cellulose-basedlow lignin-based	 high frequency (0–35 years) replacement severity surface fires 	moderate decomposition ratehigh bio-activity
Ponderosa pine	 moderate cellulose-based low to moderate lignin-based 	 high frequency (0–35 years) low severity surface/passive crown fires 	 moderate decomposition rate high bio-activity
Douglas-fir	low cellulose-basedmoderate lignin-based	 low/high frequency (35–200 years) mixed severity surface/passive and active crown fires 	 moderate decomposition rate moderate bio-activity
Lodgepole pine	low cellulose-basedmoderate lignin-based	 low frequency (100–200+ years) replacement severity active and passive crown/infrequent surface fires 	slow decomposition ratelow bio-activity
Spruce/subalpine fir	high cellulose-basedhigh lignin-based	 low frequency (>200 years) replacement severity active and passive crown/ground fires 	slow decomposition rateslow bio-activity

^a: Charcoal C sources adapted from Johnson and Miyanishi [8] which defines cellulose-based char coming from grasses, litter and small coarse woody debris (CWD) and lignin-based charcoal from sound and rotten CWD; ^b: Fire Regimes adapted from Veblen *et al.* [31] and Romme *et al.* [19]; ^c: Soil processes are not empirically-derived and are meant to represent unmeasured variables relative to the other vegetation types in the table. Zhang [32] report ecosystem decomposition rates vary by litter quality (*i.e.* lignin content), soil temperature and moisture content. Bio-activity is related to the degree of soil charcoal mixing depth with rate of mixing assumed to be lower in colder, high elevation vegetation types and higher in warmer, low elevation vegetation types [12].

Ponderosa pine mineral soils are enriched significantly with SOC compared to Douglas-fir and lodgepole pine. Ecological conditions favorable to SOC accumulation include warmer temperatures and more C input from above ground productivity and belowground root turnover. Combined with the relatively higher amounts of CC, ponderosa pine forests have the most efficient ecosystem C retention mechanisms among these vegetation types. Ponderosa pine soils were sampled to 10 cm depth only in this study hence the results are an under-estimation of the total CC pool given the deep A horizon soils that often extend below 10 cm. In contrast, high elevation montane soils store most soil CC at the surface in a shallower A horizon so this study likely sampled the bulk of that total CC pool.

Soil charcoal C pool analysis studies have been conducted in other temperate ecosystems. For example, Carcaillet and Talon [27] analyzed five transects that graded from subalpine conifer forests into alpine tundra in the French Alps. They observed an inverse relationship with less soil CC mass with increasing elevation (0.1 to 3.0 mg charcoal C ha⁻¹). Mackenzie *et al.* [4] sampled charcoal in the upper 6 cm of mineral soil in live oak woodlands (*Quercus spp.*), mixed conifer forests, and red fir (*Abies magnifica*) forests along two elevation gradients in the northern Sierra Nevada Mountains. They report that soil CC mass increased with elevation with a range of 1.0 to 5.0 mg CC ha⁻¹. DeLuca and Aplet [13] estimated 7.0 to 20.0 mg (non-cycling) C ha⁻¹ for the upper 10 cm of mineral soil in low elevation temperate conifer forests.

The overall range of CC pools (1.2 to 1.5 mg CC ha⁻¹ and 1.1 to 1.4 g CC kg⁻¹) and CC/SOC ratios (0.05–0.08) observed in these watersheds are lower than other temperate ecosystems in the western United States [4,20]. Kurth *et al.* [20] report large soil charcoal pools in surface soils (0–10 cm) for ponderosa pine forests in western Montana ranging from 2.91 to 9.17 g CC kg⁻¹. Our study area, with relatively warmer annual temperatures and thus a more rapid ecosystem decomposition rate probably retains total CC for comparatively shorter time periods [32]. Also, reduced vegetation growth resulting from less mean annual precipitation could lead to less total biomass available for charcoal conversion during a fire and thus less to contribute to soil CC pools.

The thermo-chemical digest method used here may sample a more recalcitrant portion of the BC spectrum which yields a lower estimation of this slow-cycling pool. The Kurth-Mackenzie-DeLuca (KMD) method assesses BC by degrading more labile BC formed at low temperature while retaining the more resistant charcoal and soot. One of the limitations of this method (and of most soil charcoal analysis methods) is the lack of approved laboratory standards with known quantities of charcoal that can be used for testing digest efficiency [33]. It is possible that the modified KMD method results in a more efficient digest that retains only the most recalcitrant C products. Because we used an aluminum block, the digestion flasks were surrounded by the heat source in contrast to the hotplate heat source in the original method. The low CC mass reported in this study may result in part from method differences as opposed to regional ecological conditions. Further evaluation of the modified KMD method along with development of known charcoal standards is needed to fully understand which portion of the BC spectrum was sampled.

Additional efforts to further understand soil charcoal pools in temperate conifer forests should include whole-soil profile analysis, whole-BC spectrum analysis and radiocarbon dating. Whole-profile analysis including the forest floor layer will lead to more thorough charcoal C estimation. Not sampling to depth or in the forest floor was a pre-determined limitation of this study. Sampling in the upper horizons allowed for a larger sample size across the study as a whole which

increased model strength but overlooked a possibly larger soil CC pool. This is most pronounced for ponderosa pine soils. These results should be interpreted as surface soil CC pools with the total CC pool a function of vertical distribution of charcoal C which varies by ecological factors.

Whole-BC spectrum analysis would require benzene polycarboxylic acid (BPCA) markers coupled with ¹³C Nuclear Magnetic Resonance (NMR) analysis methods that have been used in previous studies [30,34,35] and is one of the most effective methods for detecting the broadest portion of the BC spectrum [33]. If it becomes routine to analyze post-digest samples with whole-spectrum analysis, these results could be related to fire behavior or source material, which would create considerable insight for *in situ* charcoal formation. Charcoal C radiocarbon dates reveal the age of the charcoal which, combined with microscopic botanical imaging [36], would determine total residence time and the source species. Such an approach might be used to complete a paleo-ecological reconstruction of past species assemblages and fire behavior in these or other watersheds [37,38]. Knowledge of previous vegetation types and movement on a landscape as a function of shifting climatic conditions as revealed through the charcoal record may prove relevant if global climate change or local management activities continue to alter established fire regimes and vegetation distribution patterns [39].

How would global climate change (GCC) alter charcoal formation and soil charcoal pools in temperate conifer forests? Even under the current greenhouse gas emission scenario, temperatures are expected to rise in the northern hemisphere [40]. Boreal forests and temperate mountain regions are highly sensitive to such changes and later this century will become drier with a risk for more wildland fire events [39]. Westerling *et al.* [39] used results from fire—climate simulations to show that mid-elevation forests with replacement severity fire regimes in the Rocky Mountains are the most sensitive to a warming climate. Changes in fire frequency, extent, severity and seasonality are underway and are expected to continue, albeit at an increased rate. They also report potential shifts from lower montane vegetation types to shrublands but also indicate inherent uncertainty in predicting exactly what will unfold in the next century.

Increased fire frequency in temperate conifer forests should reduce the amount of available fuels over time. Subsequently, contributions to SOM and soil BC pools would decrease leading to a net decrease in total ecosystem C over time. Adger *et al.* [40] reported that net C uptake in forests is expected to peak around 2050 and then forests will become a net C source. Increasing fire frequency, declining BC pools and increasing C loss from terrestrial ecosystems could all combine to further exacerbate GCC. Future research will be needed to further our understanding of GCC and impacts to established soil BC cycles. However, without developing a current baseline of regional BC pools and fluxes it will be difficult to evaluate these impacts [41].

5. Conclusions

In summary, we show that soil CC pools in the upper 10 cm mineral soil differ across the dominant vegetation types in the Colorado Front Range based on sampling in the Bear Creek and Clear Creek watersheds. The weak bimodal pattern is an initial gain with elevation between foothills shrublands and the lower montane forest types prior to a mid-elevation decline in upper montane lodgepole pine forests before increasing again in the spruce/subalpine fir forests. This pattern is attributed to the convergence of several unique ecological and biological processes. Sampling at a watershed-scale

required a chemical analysis technique that was rapid and inexpensive to account for the hundreds of samples needed to detect statistically significant differences. The modified KMD method was effectively employed as this technique but still needs further refinement. Prior research in the Colorado Front Range on fire behavior and soil profile distribution was an aid in interpreting the empirical results from this experiment. More research is needed to determine the ecological and biological importance of these results. Future modeling and field-based efforts are called for after revealing a landscape-pattern of SOC and CC pools across these vegetation types.

Acknowledgements

We thank Kathy Green for help with statistical design.

Conflict of Interest

The authors declare no conflict of interest.

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