AGU PUBLICATIONS

JGR

Journal of Geophysical Research: Biogeosciences

RESEARCH ARTICLE

10.1002/2015JG002959

Key Points:
- Carbohydrate stocks decreased with fire severity in organic and mineral layers
- SOM stability index decreased and decomposition index increased with severity
- Past fire legacies confound interpretation of single-fire effects on SOM

Supporting Information:
- Supporting Information S1

Correspondence to:
J. R. Miesel,
mieselje@msu.edu

Citation:
Miesel, J. R., W. C. Hockaday, R. K. Kolka, and P. A. Townsend (2015), Soil organic matter composition and quality across fire severity gradients in coniferous and deciduous forests of the southern boreal region, *J. Geophys. Res. Biogeosci.*, *120*, 1124–1141, doi:10.1002/2015JG002959.

Received 12 FEB 2015
Accepted 14 MAY 2015
Accepted article online 19 MAY 2015
Published online 22 JUN 2015

Soil organic matter composition and quality across fire severity gradients in coniferous and deciduous forests of the southern boreal region

Jessica R. Miesel[1], William C. Hockaday[2], Randall K. Kolka[3], and Philip A. Townsend[4]

[1]Department of Forestry, Michigan State University, East Lansing, Michigan, USA, [2]Department of Geology, Baylor University, Waco, Texas, USA, [3]Northern Research Station, USDA Forest Service, Grand Rapids, Minnesota, USA, [4]Department of Forest and Wildlife Ecology, University of Wisconsin-Madison, Madison, Wisconsin, USA

Abstract Recent patterns of prolonged regional drought in southern boreal forests of the Great Lakes region, USA, suggest that the ecological effects of disturbance by wildfire may become increasingly severe. Losses of forest soil organic matter (SOM) during fire can limit soil nutrient availability and forest regeneration. These processes are also influenced by the composition of postfire SOM. We sampled the forest floor layer (i.e., full organic horizon) and 0–10 cm mineral soil from stands dominated by coniferous (*Pinus banksiana* Lamb.) or deciduous (*Populus tremuloides* Michx.) species 1–2 months after the 2011 Pagami Creek wildfire in northern Minnesota. We used solid-state ^{13}C NMR to characterize SOM composition across a gradient of fire severity in both forest cover types. SOM composition was affected by fire, even when no statistically significant losses of total C stocks were evident. The most pronounced differences in SOM composition between burned and unburned reference areas occurred in the forest floor for both cover types. Carbohydrate stocks in forest floor and mineral horizons decreased with severity level in both cover types, whereas pyrogenic C stocks increased with severity in the coniferous forest floor and decreased in only the highest severity level in the deciduous forest floor. Loss of carbohydrate and lignin pools contributed to a decreased SOM stability index and increased decomposition index. Our results suggest that increases in fire severity expected to occur under future climate scenarios may lead to changes in SOM composition and dynamics with consequences for postfire forest recovery and C uptake.

1. Introduction

Fire is a key ecological driver in ecosystems across the globe [*Bond and Keeley*, 2005]. Future climate scenarios predict that fire occurrence, severity, and area burned will increase due to rising regional to global temperatures and greater incidence of drought [*de Groot et al.*, 2013; *Flannigan et al.*, 2009a, 2009b], with accompanying increases in C emissions from fire [*de Groot et al.*, 2013]. Northern latitudes are expected to experience the greatest temperature increases [*IPCC*, 2007] as well as the greatest increases in fire season length and severity [*Flannigan et al.*, 2013].

Changes to fire regimes (characteristic patterns of fire frequency, intensity, severity, size, and season) [*Heinselman*, 1981], whether caused by shifts in climate or by past forest management practices, have the potential to fundamentally alter forest C dynamics relative to historic conditions by disrupting successional patterns, plant species composition [*Bond-Lamberty et al.*, 2007; *Franklin et al.*, 2005; *Scheller et al.*, 2005], and ecosystem processes [*Liu et al.*, 2011; *Turner*, 2010]. An assessment of fire effects on forest C in the western United States showed that high-severity fire causes greater tree mortality, fuel consumption, and C emissions than low-severity fire [*Ghimire et al.*, 2012]. Knowledge about the ways that changes in fire regimes will affect the composition and turnover of soil organic matter (SOM) is much more limited, although there has been growing interest in understanding relationships between fire and soil C, and the impacts of heating on organic matter composition [see reviews by *Certini*, 2005; *Gonzalez-Perez et al.*, 2004; *Knicker*, 2007, and references therein]. To date, relatively few publications have reported within-fire comparisons of fire severity on SOM composition and dynamics. This topic represents a critical knowledge gap because SOM plays an important role in postfire forest C dynamics by influencing nutrient cycling, short- and long-term nutrient availability, C feedbacks to the atmosphere, and ultimately C uptake by a recovering forest.

The magnitude of fire impacts on an ecosystem is a function of fire temperature and rate of spread, which in turn are influenced by topography (such as slope and aspect), weather (such as air temperature, relative humidity, and drought condition), and fuel characteristics (such as type, mass, spatial arrangement, and moisture content) [*Keeley*, 2009]. Considerable variation in the magnitude of impact may occur within individual wildfires. Interest in accounting for the heterogeneity in fire effects has been increasing, with recent publications addressing heterogeneity of ecosystem components in a southern mixed pine/hardwood forest [*Brown et al*., 2014], of charcoal content in mixed conifer forest [*Heckman et al*., 2013], and of total soil C and N in mature Douglas fir (*Pseudotsuga menziesii* var. *menziesii* (Mirb.) Franco) forest [*Homann et al*., 2011]. However, the metrics used to classify fire severity to date have not been consistent across ecosystem types, forest strata, and disciplines [see *Ghimire et al*., 2012; *Jain et al*., 2012, and references therein]. Accounting for the heterogeneity of fire effects within fires will be important for understanding relative differences in fire effects across fire severities and for anticipating the magnitude and scale of effects under predicted increases in future fire severity. In addition to impacts on soil C content, increases in fire severity will have implications for soil SOM composition and C cycling in forests after fire.

Interest in characterizing the composition of soil organic matter has also increased in recent years as the limitations of current ecosystem C models have become more apparent. In general, fire increases the compositional heterogeneity of SOM and the stability of soil C by producing polyaromatic biopolymers during charring (i.e., smoldering combustion, or heating with limited to no oxygen availability) [*Knicker*, 2007]. These polyaromatic structures are broadly termed “pyrogenic” C (PyC) and are considered to be more resistant to microbial decomposition and thus contribute to longer SOM mean residence times relative to SOM unaltered by fire [*Lehmann et al*., 2006; *Schmidt et al*., 2011]. However, the limited data that exist for PyC formation and cycling as well as the large variability in PyC concentrations and environmental conditions in natural systems [*DeLuca and Aplet*, 2008; *Kasin and Ohlson*, 2013; *Lehmann et al*., 2011; *Masiello*, 2004; *Preston*, 2009] contribute to only rudimentary representation in ecosystem C models [*Liu et al*., 2011]. Failure to incorporate the influence of specific SOM components such as PyC in C models may limit model accuracy and predictive ability [*Deluca and Boisvenue*, 2012; *Lehmann et al*., 2008; *Woolf and Lehmann*, 2012]. However, the factors that drive PyC formation and function in natural settings remain difficult to characterize.

Linking fire effects to changes in SOM abundance and composition is needed to improve predictions of ecosystem C cycle response to changing fire regimes [*Schmidt et al*., 2011; *Todd-Brown et al*., 2013]. Previous evaluations of differences in fire effects due to fire severity or intensity have compared fire effects between forest types [*van Bellen et al*., 2010] or between wildfire sites [*Knicker et al*., 2006]. Interest in understanding the factors that influence soil black C (i.e., pyrogenic organic matter, char, and charcoal) has been increasing in recent years. For example, a study in a mixed conifer forest in Oregon, USA, evaluated differences in soil C conversion to charcoal among C pools, using fire severity categories determined by percent survival of aboveground vegetation [*Heckman et al*., 2013]. An earlier study at the same site found that soil C and N losses were greater in areas burned at high severity than those burned at moderate to low severity, using severity categories determined from overstory tree mortality and lidar-estimated canopy mortality [*Homann et al*., 2011]. Few publications to date have made use of natural variability in severity within a site for the purpose of studying severity-induced changes in the chemical composition of the SOM.

The 2011 Pagami Creek wildfire in northern Minnesota, USA, provided an ideal opportunity to evaluate fire effects on forest SOM composition across a gradient of fire severity, for two forest cover types that are common in the southern boreal forest. Our overarching objective is to evaluate how shifts in fire severity will influence the content and composition of belowground forest C. Here we address three research questions. How does postfire SOM composition vary (1) along a gradient of fire severity, (2) between contrasting prefire forest cover types, and (3) between the forest floor layer (i.e., organic horizon) and the upper mineral soil? These data are relevant for understanding the spatial heterogeneity of within-fire effects on ecosystem properties, and for anticipating longer-term impacts on SOM cycling and C flux to the atmosphere. This study is the first to our knowledge to evaluate within-fire differences in fire severity effects on SOM for two stand types with contrasting prefire species composition.

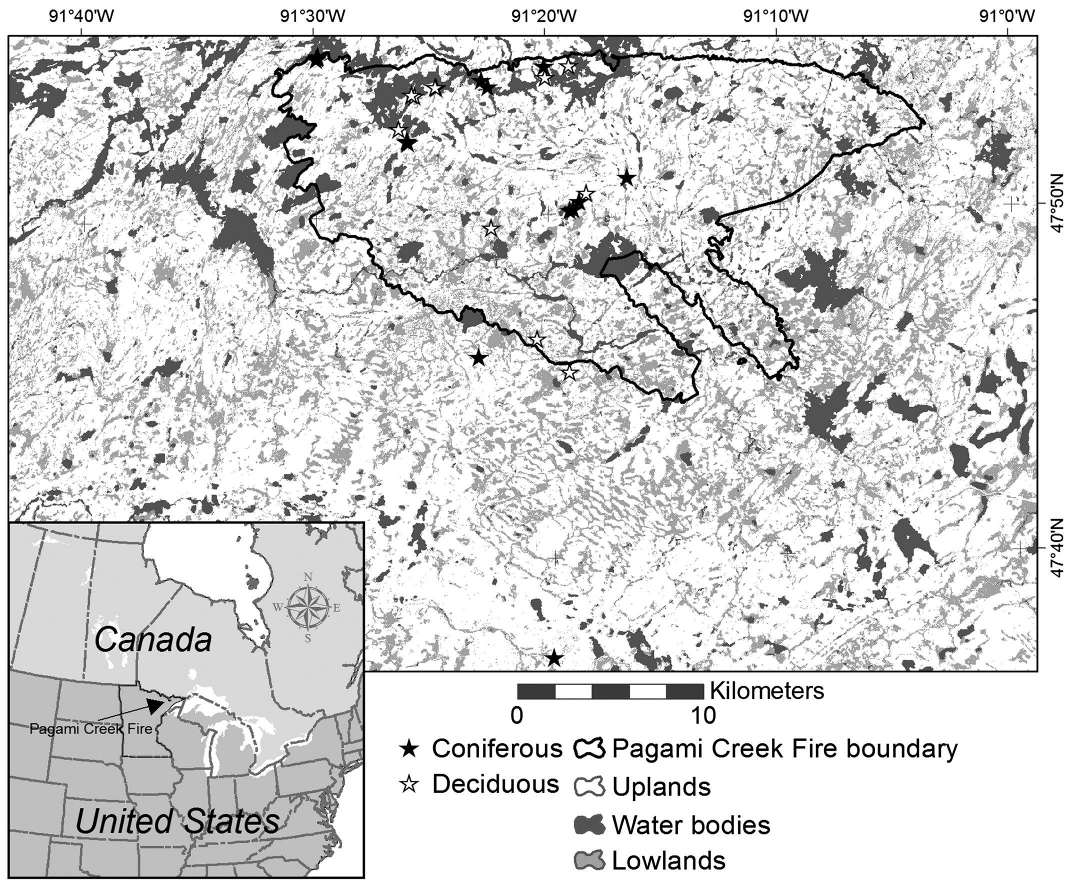

Figure 1. Map of the Pagami Creek wildfire perimeter. Inset shows location in northern Minnesota, USA. Filled stars indicate coniferous plots, and open stars indicate deciduous plots.

2. Methods

2.1. Study Site

The Pagami Creek wildfire occurred in the Boundary Waters Canoe Area Wilderness (BWCAW) in northern Minnesota, USA (Figure 1), as a result of a lightning strike on 18 August 2011. The Pagami Creek fire burned a total of 37,000 ha between 18 August and 22 October and was the largest wildfire in Minnesota since 1918. The landscape supports a complex matrix of lakes, wetlands, and upland coniferous and deciduous forests in which fire is a key natural disturbance. The BWCAW is a unique study site in that it has a well-documented fire history with identified stand origin dates as early as 1595 CE. During the presettlement period (1727–1868), fires in the BWCAW occurred on average at 4.3 year intervals, and major fires (i.e., fires that burned $\geq$259 km^2) occurred at 28 year intervals. The average interval between fires increased to 6.1 years for the 1911–1972 time period, during which no major fires were recorded [*Heinselman*, 1996]. The change in fire occurrence corresponds to widespread implementation of U.S. fire suppression policies that began in the early 20th century soon after the establishment of the U.S. Forest Service; these policies mandated the “protection from forest fires” as “the first measure necessary for the successful practice of forestry” [*Muir*, 1941; *Pyne*, 1982]. Fire suppression in the Superior National Forest began in 1910; prior to this time period, the BWCAW experienced fires even in years that were not characterized by regional drought [*Heinselman*, 1996]. Mean temperatures for the area are −8°C for January and 17°C for July, with 71 cm of mean annual precipitation. Soils in this area are poorly developed and are derived primarily from glacial till and outwash from the Wisconsin glacial period. Upland soils are entisols classified as well-drained, shallow (20–50 cm) gravelly coarse sandy loam over bedrock (Quetico (Lithic Udorthents) and Insula (Lithic Dystrudepts) series) or moderately deep (50–100 cm) gravelly sandy loam over bedrock (Conic (Typic Dystrudepts) and Wahlsten (Oxyaquic Dystrudepts) series) (J. Barott, Soil

Table 1. Summary of Key Characteristics Used to Determine Fire Severity Level and Number of Coniferous and Deciduous Plots Used for Soil Organic Matter (SOM) Characterization in This Study[a]

Severity Index	Severity Description	Plots (*n*) Coniferous	Plots (*n*) Deciduous
0	Unburned	2	1
1	Lightly burned; surface organic matter >85% present	1	1
2	Moderately burned; surface organic matter 40–85% present	0	1
3	Severely burned; surface organic matter <40% present	2	0
4	Severely burned; little to no surface organic matter present	1	1

[a]Soil-level fire severity classification followed *Jain et al.* [2012]. Samples used for SOM characterization were composites of samples from three subplots per plot for the forest floor layer and (separately) for the 0–10 cm mineral soil.

Scientist, USFS Superior National Forest, personal communication). A more detailed description of the study site and the Pagami Creek wildfire has been presented previously [*Kolka et al*., 2014].

2.2. Experimental Design and Soil Sampling

As part of the larger investigation [*Kolka et al*., 2014], we used knowledge of prefire vegetation [*Wolter and Townsend*, 2011; *Wolter et al*., 2009] and remotely sensed estimates of fire severity (relative differenced normalized burn ratio) [*Miller et al*., 2009] to establish a series of transects and plots to capture gradients in expected fire severity. However, fire severity was assessed in the field (see details below), and these field-based severity estimates were used to designate the classifications we report in this study. Our plot design was similar to that of the U.S. Forest Service's Forest Inventory and Analysis (FIA) program [*FIA*, 2011, 2012]. All areas sampled in this study were located in naturally regenerated forest that had originated after wildfire between 101 and 147 years before the 2011 Pagami Creek fire (*Heinselman* [1996] and Fire History database available from Superior National Forest, Ely, WI) (Table S1 in the supporting information).

Here we present results from samples of the forest floor layer and mineral soil (0–10 cm) collected within 1–2 months (October–November 2011) after fire, immediately before winter snowfall began, and from samples from supplemental plots established in the spring of 2012 immediately following snowmelt. We established the supplemental plots in spring because the onset of winter terminated field sampling in the autumn after the fire. The supplemental plots were established as part of the original, larger investigation to increase the number of unburned reference sites within the fire perimeter. Snowmelt is unlikely to affect soil organic matter content in unburned areas at this site because the area lacks steep topography and surface material is not eroded during spring runoff. Across all severity levels, we installed 123 plots in upland forest types over the first year following fire. We assessed forest type in each plot based on a visual assessment of trees that remained standing after the fire and those that had likely fallen during or after the fire. For the present analysis, we selected upland plots that were dominated by jack pine (hereafter coniferous) or aspen (*Populus tremuloides* Michx., hereafter deciduous).

We assessed the postfire environment using a fire severity indicator for each plot in the field at three 10 m^2 circular subplots per plot by establishing one subplot at 6.5 m from the plot center along each of three transects orientated 0° (north), 120°, and 240° from the plot center. Fire severity assessments followed a detailed postfire soil classification protocol established from a synthesis of literature reporting fire effects on soil and vegetation [*Jain and Graham*, 2007; *Jain et al*., 2012]. This method classifies fire severity based on the surface cover of the forest floor layer remaining and the oxidation level (indicated by soil color) of the mineral soil. We estimated the percent cover of the residual forest floor layer and mineral soil color, on each subplot, and aggregated across subplots to develop a plot-level fire severity estimate. We compared severity levels using the main categories only. Main fire severity categories determined using soil-level characteristics are given in Table 1.

We collected forest floor and mineral soil samples near each subplot described above, at 3.7 m from the plot center along the same azimuths used to assess soil-level fire severity. We collected the full forest floor layer within a 30 cm diameter sampling frame, and we used a 5 cm inner diameter hammer-driven bulk density corer to sample the 0–10 cm mineral soil layer within the sampling frame, unless we encountered a limiting layer such as bedrock at <10 cm depth. All 0–10 cm mineral soil samples collected for this study consisted of a full 10 cm core: if we encountered a limiting layer or large rocks at <10 cm depth, we collected the mineral soil sample at a distance of ≤0.5 m from the forest floor layer sample location. We froze the triplicate forest floor layer and mineral soil samples after returning to the laboratory and then aggregated the triplicate samples into a plot-level sample before drying (65°C for forest floor samples and 105°C for mineral soil samples) and analysis.

The Pagami Creek fire fortuitously burned over five Forest Inventory and Analysis (FIA) plots that had been established and measured in 2001–2002 by FIA program personnel [*FIA*, 2011, 2012]. Although comparisons of prefire and postfire data are rare for wildfire sites, the preexisting soil data from these FIA plots enabled us to evaluate changes in prefire forest C and N concentrations and C:N ratio on five individual plots. We used forest floor and 0–10 cm mineral soil data from the 2001–2002 sampling of these plots to provide the best available data on prefire forest soil C and N. Because soil C and N concentrations could vary on annual timescales, we are unable to evaluate what effect, if any, inter-annual variability in C and N concentrations has on the differences we report between prefire and postfire measurements. All FIA plots burned by the 2011 fire were classified as severity class 3 or 4, and all supported coniferous forest cover: four were dominated by jack pine (*Pinus banksiana* Lamb.), and one was dominated by black spruce (*Picea mariana* (Mill.) Britton, Sterns & Poggenb.) and a mixture of other species. Data for the spruce-dominated plot fell within the range of data from jack pine-dominated plots, and we included this plot to provide the best available data from the range of prefire conditions. No analogous prefire FIA data exist for deciduous plots. To evaluate differences in SOM composition across severity levels, we used unburned plots within or adjacent to the wildfire site as a reference for burned plots, for each forest cover type (coniferous or deciduous).

2.3. Laboratory Analysis

2.3.1. Combustion Elemental Analysis

We ground forest floor samples in a stainless steel Wiley mill with complete cleaning between samples, before analysis for total C and N on a LECO Total Elemental Analyzer (St. Joseph, MI). Mineral soil samples were passed through a 2 mm sieve and pulverized before analysis. We use total C concentrations to report organic C concentrations because mineral soil samples fumigated with HCl prior to combustion analysis [*Harris et al.*, 2001] showed a <1% difference in C concentrations between samples before and after fumigation.

2.3.2. Carbon-13 Nuclear Magnetic Resonance

We characterized SOM in the total remaining postfire forest floor layer, and in the <2 mm size fraction in mineral soil using ^{13}C nuclear magnetic resonance (^{13}C NMR). For NMR analysis, we randomly selected a subset of available plots from each severity level and forest cover type, using plots for which both forest floor layer and mineral soil samples existed (Table 1). Iron-rich particles were detected in the forest floor layer as well as mineral soil samples, so we treated both types of samples four times with 10% HCl/HF solution [*Gelinas et al.*, 2001] prior to NMR analysis. The HF treatment improves NMR signal to noise ratio and quantitation by removing mineral material and paramagnetic iron oxides [*Smernik and Oades*, 2000a]. Although HF treatment has been reported to cause 7% to 23% loss of initial C content and may cause changes in composition of polysaccharide and lignin molecules, the treatment does not cause appreciable changes in bulk SOM composition determined by NMR [*Gelinas et al.*, 2001; *Rumpel et al.*, 2006]. We acquired NMR data on a 300 MHz Bruker Avance II spectrometer using a 7 mm magic angle spinning probe. We packed approximately 250 mg of HF-treated soil (dried and pulverized) into a 7 mm zirconia rotor, sealed with a Kel-F cap. Cross-polarization (CP) and direct polarization (DP) spectra were collected while spinning at a rate of 5 kHz. The direct polarization magic angle spinning (DPMAS) spectra were acquired using a 90° excitation pulse (75 MHz), followed by a series of four rotor-synchronized 180° pulses for total suppression of spinning sidebands (TOSS), two-pulse phase-modulated (TPPM) proton decoupling, and a recycle delay of ≥100 s. The cross-polarization magic angle spinning (CPMAS) spectra were acquired after a 90° ^{1}H pulse, with spinning sideband suppression (TOSS) and TPPM proton decoupling and a recycle delay of ≥3 s. All pulses were calibrated and Hartman-Hahn matching conditions were determined using crystalline glycine as an external standard. The spectra were zero filled and exponentially multiplied, and line broadening was applied before phasing and baseline correction. We applied 50 Hz line broadening to CPMAS data and 70 Hz line broadening to DPMAS data. Additionally, DPMAS spectra were background subtracted to remove signals from carbon-containing components of the probe and rotor [*Smernik and Oades*, 2001]. We recorded between 7200 and 23,000 scans for CPMAS and between 560 and 3450 scans for DPMAS. We then executed an algorithm to integrate the spectral magnitude in the following frequency ranges: 0–45, 45–60, 60–95, 95–110, 110–145, 145–165, 165–185, and 185–220 ppm.

We used spin counting experiments to evaluate the percentage of soil organic carbon (SOC) observed (C_{obs}) in our NMR spectra [*Smernik and Oades*, 2000b] (supporting information). Previous studies have shown that cross-polarization magic angle spinning (CPMAS) underestimates PyC content in soils because the remote protonation and rapid $T_{1\rho}H$ relaxation of charcoal results in low observability (C_{obs}) in CPMAS spectra. In this study, the CPMAS signal intensities have not been corrected for signal loss due to $T_{1\rho}H$ relaxation rates. Therefore, the C_{obs} values for CP spectra represent a conservative estimate of the SOC observed. The DPMAS method was used here because it is known to be more reliable in the detection of a wide range of PyC, from slightly charred material to highly aromatic compounds [*Baldock and Smernik*, 2002; *Kane et al.*, 2010].

2.3.3. Molecular Mixing Model

Our use of ^{13}C NMR spectroscopy enables an estimate of fire severity effects on the major components of soil organic matter: carbohydrates, proteins, lignins, lipids, and charcoal (PyC). The oxidation of organic compounds during decomposition leads to the formation of carbonyl C (aldehyde, ketone, and acid functional groups), which is also discernable by ^{13}C NMR. This information provides a valuable indication of changes to organic matter composition—and potential impacts on organic matter cycling following fire—across a range of fire severities and two forest types. We input the NMR spectra peak areas into a molecular mixing model (MMM) [*Baldock et al.*, 2004] to estimate the contribution of PyC and other major classes of organic compounds relative to total SOC, for CPMAS and DPMAS experiments. The MMM calculations for N-containing components (protein and PyC) were additionally constrained by the C and N concentrations measured in each sample after HF treatment. The squares of deviation of NMR peak areas (measured versus modeled) were used as a means of assessing "goodness of fit." We accepted the model results if the sum of squares for these samples was <4% of the total spectral area.

2.4. Calculations and Statistical Approach

The long-term stability of SOM is considered to be an ecosystem property, depending upon the chemical quality of organic inputs to soil and a multitude of factors affecting soil climate, habitat, and heterotroph communities [*Schmidt et al.*, 2011]. Although it is beyond the scope of this investigation to provide predictions of SOM stability, our NMR data are amenable to a proxy-based assessment of the inherent chemical stability of the SOM and its degree of decomposition. Lignin in our study is estimated from NMR data and the MMM and refers to the biopolymer produced by higher plants [*Baldock et al.*, 2004] rather than to acid-insoluble residue (AIR) that has been traditionally referred to as "lignin" [see *Marín-Spiotta et al.*, 2014, and references therein]. The lignin:N ratio has been widely applied to litter layers and surface soils as an index of organic matter stability in which higher lignin to nitrogen ratios indicate a potentially more stable organic matter [*Melillo et al.*, 1989]. Although the index developed by *Melillo et al*. [1989] was developed using the traditional understanding of lignin as AIR identified after sequential chemical fractionation, our use of the lignin:N ratio relies on the lignin pool estimated from NMR and the MMM, and as such, our use of lignin excludes contribution from condensed tannins and cutins that are present in AIR [*Hilli et al.*, 2012; *Leary et al.*, 1986; *Preston et al.*, 2009]. As an antithetical to the stability index, the ratio of alkyl C to O-alkyl C peak areas is a proxy for the extent of decomposition [*Baldock et al.*, 1997]. Higher values for the alkyl to O-alkyl ratio indicate greater extent of decomposition. We calculated the ratio of lignin to N from DPMAS NMR, MMM, and elemental analysis results. The ratio of alkyl C to O-alkyl C was calculated from CPMAS NMR data because the CP method is more sensitive to changes in these functional groups than is the DP method.

We used general linear models to test for differences in fixed effects (fire severity, forest type, and their interaction) for forest floor layer and mineral soil C and N concentrations and stocks, and C:N ratio measured by elemental analysis. All analyses were performed with SAS software using the MIXED procedure (SAS software, version 9.3, SAS Institute, Inc., Cary, NC, USA). Data for the forest floor layer and mineral soil percent C and C and N stocks were log transformed before analysis. Data for forest floor C:N ratio and mineral soil percent N and C:N ratio were ranked before analysis. We report statistical significance at $p < 0.05$ unless otherwise indicated.

Table 2. Forest Floor Layer and 0–10 cm Mineral Soil Carbon (C) and Nitrogen (N) Concentrations and Stocks, C:N Ratio, and Forest Floor Thickness for Five Coniferous-Dominated Forest Inventory and Analysis (FIA) Plots Burned by the 2011 Pagami Creek Fire[a]

Depth	Severity	Measurement	*N*	Prefire (FIA Data)	Postfire (This Study)	Change (%)
Forest floor	3 + 4	Forest floor thickness (cm)	5	8.74 (2.05)	2.12 (0.50)	−76
		C (%)	5	41.03 (4.18)	17.25 (4.22)	−58
		N (%)	5	1.48 (0.18)	0.94 (0.24)	−36
		C:N	5	28.56 (3.06)	18.89 (2.42)	−34
		C stock ($g\ m^{-2}$)	5	1356.35 (229.90)	549.72 (140.21)	−59
		N stock ($g\ m^{-2}$)	5	47.77 (6.09)	32.11 (9.45)	−33
Mineral soil, 0–10 cm	3 + 4	C (%)	5	17.34 (9.16)	4.60 (0.97)	−73
		N (%)	5	0.47 (0.14)	0.28 (0.05)	−40
		C:N	5	30.59 (7.36)	16.54 (0.52)	−46
		C stock ($g\ m^{-2}$)	4	2897.91 (783.50)	2667.24 (280.25)	−8
		N stock ($g\ m^{-2}$)	4	92.41 (5.00)	159.41 (15.69)	73

[a]Prefire data are from FIA samples taken in 2001/2002, and postfire data are from this study. Shown are mean (SE) for plots classified as fire severity class 3 ($N = 2$) and class 4 ($N = 3$ or $N = 2$ for mineral soil due to missing FIA data) combined. Percent change is shown for postfire data relative to prefire data.

We calculated total C stocks using measured C concentrations and forest floor weight and mineral soil bulk density measured for all coniferous and deciduous plots. We calculated stocks for each SOM component for each forest cover type and fire severity level in the same way, using the concentrations of each SOM component determined from DPMAS NMR and the mean bulk density of all plots of the same soil layer and severity level within forest type. Because of the long acquisition time of DPMAS NMR spectra and the limited availability of replicate plots for some combinations of severity level and forest type, we chose to acquire spectra for samples representing a range of severities for composited triplicate samples for each of the two forest cover types rather than for replicate plots within severity level. We present the estimates of SOM stocks as a framework for further investigations of how future changes in fire severity may impact the composition of SOM and the relative stability of postfire C pools in forest soil.

3. Results

3.1. Prefire and Postfire Data From FIA Plots

Relative to prefire FIA measurements taken in 2000–2001 in conifer-dominated plots, we observed decreases in postfire forest floor layer thickness and in forest floor and 0–10 cm mineral soil C and N concentrations, C:N ratios, and C stocks, whereas we observed a 73% increase in 0–10 cm mineral soil N stock (Table 2). The greatest change we observed relative to prefire conditions was in forest floor layer thickness (−76%), whereas the smallest change was in 0–10 cm mineral soil C stock (−8% change overall; however, the small magnitude of overall response resulted from wide variability in the available data which includes a −34% loss for severity level 3 and +49% increase for severity level 4). The mineral soil C stock was the only variable for which we observed a different response for the severity level 3 versus severity level 4 FIA plots. These changes represent magnitude of difference between prefire (FIA data) and postfire (our data) values and were not tested for statistically significant differences because of the small sample size.

3.2. Soil Organic Matter Composition Across Severity Levels and Between Forest Cover Types

The NMR spectra reveal a greater response to fire severity level in the forest floor layer than in the mineral soil, for both the coniferous and deciduous cover types. The relative contribution of the aromatic region to total signal intensity increased in severity levels 3 and 4 for the coniferous forest floor layer and in severity levels 1 to 4 for the deciduous forest floor, relative to the unburned controls (Table 3 and supporting information Figures S1 and S2). The CPMAS spectra show no corresponding increases in the relative contribution of the aromatic region in mineral soil for either forest type; however, the DPMAS spectra—which reflect more accurate quantitation of organic C moieties—show 23% to 40% increases in the aromatic region of deciduous mineral soil, relative to the control. The only major increase in the contribution of the aromatic region we observed in the coniferous mineral soil occurred in severity level 3 (24% increase

Table 3. Contributions (% of Total Signal Intensity) of the Chemical Shift Regions of ^{13}C CPMAS and DPMAS NMR Spectra of the Forest Floor Layer (i.e., Entire Organic Horizon, FF) and 0–10 cm Mineral Soil from Coniferous and Deciduous Cover Types, by Severity Level[a]

			Relative Contribution (%) of Chemical Shift Region (ppm)							
				O-Alkyl C			Aryl C		Carboxyl C/Amide/Ester	
			Alkyl C	Methoxyl/N-alkyl	O-Alkyl	Di-O-Alkyl	Aromatic	Phenolic	Carboxyl/Amide	Aldehyde/Ketone
Cover Type	Horizon	Severity	0–45	45–60	60–95	95–110	110–145	145–165	165–185	185–220
					CPMAS					
Coniferous	FF	0	20.9 (2.3)	7.8 (0.3)	32.8 (2.1)	8.8 (1.0)	17.2 (2.2)	6.6 (0.8)	4.5 (0.7)	1.4 (0.1)
		1	25.0	7.0	28.2	6.9	17.8	7.5	5.0	3.6
		3[b]	20.2 (0.2)	3.1 (0.5)	11.5 (1.9)	5.9 (0.1)	38.6 (2.4)	11.6 (0.0)	5.2 (0.2)	4.0 (0.4)
		4	14.4	1.0	7.2	5.3	51.1	10.9	5.1	5.1
	0–10	0	28.4 (0.6)	6.1 (0.6)	23.0 (5.1)	6.7 (0.6)	18.3 (2.6)	7.4 (1.2)	7.2 (0.7)	2.9 (1.2)
		1	29.5	8.3	23.4	7.25	17.4	6.4	6.54	1.2
		3[b]	26.6 (0.0)	7.7 (0.4)	23.4 (0.2)	7.4 (1.0)	17.7 (1.2)	7.5 (0.1)	7.5 (0.1)	2.4 (0.8)
		4	36.2	6.7	18.5	6.5	17.6	6.8	6.7	1.1
Deciduous	FF	0	27.5	8.0	28.5	7.0	15.3	6.7	5.6	1.3
		1	18.6	6.4	16.2	7.5	33.9	9.2	6.2	2.0
		2	22.0	3.8	13.8	6.9	36.1	9.9	4.8	2.6
		4	27.1	5.2	18.0	5.9	27.4	8.2	5.8	2.5
	0–10	0	26.6	7.6	24.1	7.8	18.2	5.4	8.5	1.9
		1	30.1	6.8	18.7	6.7	22.9	6.0	7.0	1.9
		2	20.9	6.9	21.5	9.7	21.0	9.4	8.9	1.7
		4	25.3	7.1	20.3	7.4	20.4	7.5	9.8	2.2
					DPMAS					
Coniferous	FF	0	20.4 (1.8)	8.4 (2.9)	30.0 (0.4)	8.2 (1.1)	14.5 (2.8)	9.3 (0.7)	7.1 (0.3)	2.1 (1.1)
		1	12.5	10.2	33.0	8.1	9.1	13.0	13.0	1.3
		3	5.8 (0.3)	4.8 (0.2)	2.6 (1.0)	5.9 (1.0)	57.1 (0.8)	14.3 (1.5)	7.4 (0.4)	2.1 (0.4)
		4	4.7	4.5	2.5	3.7	56.6	15.8	8.3	3.9
	0–10	0	19.8 (2.8)	7.4 (2.2)	17.2 (2.4)	8.1 (0.3)	24.8 (3.8)	10.1 (1.3)	10.5 (0.5)	2.2 (1.6)
		1	14.5	10.5	20.1	6.5	19.1	15.4	13.7	0.2
		3[b]	19.0	8.4	10.5	9.5	30.8	9.8	10.5	1.6
		4	22.8	8.3	14.4	5.0	21.9	11.6	15.9	0.2
Deciduous	FF	0	26.4	5.0	27.1	6.9	15.6	6.0	10.9	2.1
		1	7.1	2.1	8.6	7.7	44.3	15.3	11.0	4.0
		2	9.5	5.6	2.4	7.8	52.3	12.8	7.5	2.2
		4	14.8	5.5	4.0	4.6	42.6	14.6	10.1	4.0
	0–10	0	23.0	6.0	19.8	4.9	20.9	8.0	13.2	4.1
		1	18.0	7.8	18.3	7.0	25.7	10.4	10.3	2.5
		2[c]	20.9	6.9	21.5	9.7	21.0	9.4	8.9	1.7
		4	20.9	4.6	14.3	10.6	26.5	8.5	13.4	1.3

[a]Variability within severity level is shown for coniferous forest type where values shown represent mean (SE) of replicate plots ($N = 2$ for severity 0 and 4 and $N = 3$ for severity 3).
[b]For coniferous severity 0 and severity 3 soil samples, CPMAS values show mean (SE) for $n = 2$ plots, each representing a composite of three subplot samples. We were unable to obtain a DPMAS signal for one of these plots because of very low C concentrations in the HF-treated sample.
[c]For the deciduous 0–10 cm mineral soil sample classified as severity level 2, we present CPMAS data in place of DPMAS data because we were unable to obtain a satisfactory signal for this sample due to low C concentrations.

relative to the control). In general, the chemical shifts were consistent in the forest floor layer regardless of forest cover type and were greater in the deciduous mineral soil than in the coniferous mineral soil. There does not appear to be a consistent direct relationship between fire severity level and the magnitude of response observed in the NMR chemical shift regions, beyond a general increase in the aromatic region in forest floor layers of burned areas.

3.3. C and SOM Component Stocks

Forest floor layer C stocks decreased in burned areas classified as severity levels 1, 2, and 3, and there were no statistically significant differences between unburned and severity level 4 areas, across both forest types (Tables 4 and 5). There were also no statistically significant effects of severity level or forest type on mineral soil C stocks or forest floor C or N stocks (Tables 4 and 5).

Table 4. Sampling Depth for Forest Floor (i.e., Forest Floor Thickness) and Mineral Soil Horizons, Carbon (C) and Nitrogen (N) Concentrations, and Stocks and C:N Ratio of Soils Representing a Gradient of Fire Severity in All Coniferous (Jack Pine-Dominated) and Deciduous (Aspen-Dominated) Forest Plots Sampled After the 2011 Pagami Creek Fire[a]

Cover Type	Horizon	Severity	N	Depth (cm)	C (%)	N (%)	C:N	C stock (g m^{-2})	N stock (g m^{-2})
Coniferous	FF	0	5	5.41 (1.83)	41.85 (1.57)	1.19 (0.07)	35.77 (2.25)	1871.40 (674.53)	53.60 (19.79)
		1	2	2.13 (0.63)	33.94 (0.13)	1.56 (0.12)	25.25 (5.11)	369.50 (102.50)	16.00 (7.00)
		2	7	2.13 (0.47)	21.30 (3.24)	1.00 (0.16)	22.33 (2.10)	557.86 (166.41)	25.43 (6.27)
		3	14	1.64 (0.25)	20.19 (2.20)	0.85 (0.10)	24.39 (1.37)	569.64 (104.96)	23.93 (4.46)
		4	8	1.82 (0.20)	18.29 (2.58)	0.77 (0.07)	23.19 (2.08)	688.00 (138.54)	28.13 (3.76)
	0–10	0	5	10.00	5.32 (1.59)	0.22 (0.07)	30.60 (6.70)	2924.20 (706.48)	115.20 (32.42)
		1	2	10.00	4.21 (0.31)	0.24 (0.04)	17.65 (1.65)	2742.50 (691.50)	153.00 (25.00)
		2	6	10.00	2.91 (0.42)	0.16 (0.02)	18.28 (1.48)	1874.67 (137.66)	107.00 (13.74)
		3	12	10.00	4.60 (0.53)	0.25 (0.03)	19.09 (0.86)	2792.75 (225.21)	149.58 (13.67)
		4	8	10.00	5.05 (0.95)	0.29 (0.05)	17.35 (0.61)	2768.13 (367.43)	159.25 (19.52)
Deciduous	FF	0	3	5.94 (2.13)	41.47 (1.83)	1.45 (0.15)	29.19 (2.83)	1930.67 (902.35)	66.33 (27.70)
		1	9	1.60 (0.30)	23.56 (2.80)	1.30 (0.16)	20.36 (2.22)	435.56 (89.85)	24.22 (4.72)
		2	8	2.34 (0.50)	21.70 (4.44)	1.10 (0.21)	19.33 (1.48)	461.63 (79.33)	23.75 (3.31)
		3	6	1.39 (0.27)	24.40 (6.73)	1.01 (0.09)	24.51 (6.69)	427.50 (79.92)	24.17 (4.70)
		4	2	1.52 (0.40)	19.37 (1.20)	1.17 (0.15)	16.64 (1.17)	686.50 (4.50)	41.50 (2.50)
	0–10	0	3	10.00	4.93 (1.36)	0.24 (0.07)	20.83 (0.73)	3311.67 (848.92)	159.67 (41.37)
		1	8	10.00	3.08 (0.23)	0.20 (0.02)	15.94 (1.02)	2027.00 (112.97)	128.88 (7.23)
		2	7	10.00	5.52 (1.62)	0.28 (0.08)	18.78 (1.61)	2955.17 (659.93)	155.83 (30.07)
		3	6	10.00	3.31 (0.48)	0.20 (0.02)	16.53 (1.39)	2304.67 (101.91)	145.33 (15.58)
		4	2	10.00	2.57 (0.45)	0.20 (0.06)	13.75 (2.15)	1695.50 (463.50)	132.00 (54.00)

[a]Shown are N and untransformed means (SE) of plots for each forest type, for the forest floor layer (FF), and 0–10 cm mineral soil.

When C stocks were summed across forest floor and mineral soil layers, deciduous forest showed a trend of decreasing total C with fire severity, whereas there was no trend evident in coniferous forest (Figure 2). Moderate- and high-severity fire resulted in a nonsignificant decrease in forest floor C stocks of >63% in all severity levels in both forest types, relative to unburned plots. The magnitude of loss of C stock in the coniferous forest floor decreased with severity level, whereas deciduous forest floor showed similar losses across severity levels 1 to 3 (76% to 78%) and a lesser decrease (64%) at the highest severity, level 4 (Figure 2 and Table 4). In contrast, coniferous mineral soil showed much lesser losses of C ranging from 4% to 36% and the greatest loss occurred in severity level 2 (Figure 2 and Table 4). Deciduous mineral soil exhibited nonsignificant losses in C stocks of 11% to 49%, and we observed the greatest losses at the lowest and highest severity levels (Figure 2 and Table 4). In general, deciduous mineral soil exhibited greater losses in C stocks than did coniferous mineral soil.

The C:N ratio of the forest floor decreased in all burned areas and was greater in coniferous forest than in deciduous forest (Tables 4 and 5). There were no effects of fire severity or forest type on C or N concentrations in the 0–10 cm mineral soil layer (Tables 4 and 5). The interaction between fire severity and forest type for C and N concentrations was also not significant. Across forest types, mineral soil C:N ratios were decreased by fire relative to unburned plots, and there were no differences among severity levels. C:N ratios were greater in coniferous forest than in deciduous forest across severity classes, and the interaction between severity and forest type was not significant (Tables 4 and 5). Across both forest cover types, forest floor thickness decreased in all severity levels relative to the unburned plots, although there were no statistically significant differences in forest floor thickness among burned severity levels (Tables 4 and 5).

The composition of unburned coniferous forest floor and mineral soil SOM was dominated by carbohydrates and lignin, whereas carbohydrates and lipids contributed the greatest proportion of SOM in deciduous forest floor and mineral soil, respectively (Figure 2 and Table 6). In contrast, the SOM composition in the highest burn severity in coniferous forest was dominated by PyC in the forest floor and by lignin, carbonyl groups, and protein in the mineral soil. The SOM composition in the highest severity class for deciduous forest was dominated by PyC and lignin in forest floor and mineral soil layers (Figure 2 and Table 6). We observed a near-total to total loss of forest floor carbohydrate pools in severity levels 3 and 4 in coniferous forest and in severity levels 2 and 4 in deciduous forest, whereas smaller losses occurred in the mineral soil (Figure 2

Table 5. Table of *F* and *p* Values for General Linear Models Using Fire Severity, Forest Type, and Their Interaction as Fixed Effects or Determining Statistical Significance in Differences Among Main Effects for C and N Concentrations and C:N Ratios in the Forest Floor Layer and 0–10 cm Mineral Soil in Samples from All Coniferous and Deciduous Cover Types Sampled After the 2011 Pagami Creek Fire[a]

					Severity					Forest Cover Type	
Horizon	Variable	Main Effect	*F*	*p*	0	1	2	3	4	Coniferous	Deciduous
FF	Thickness (cm)[b]	Severity	3.95	**0.018**	a	b	b*	b	b	--	--
		Forest type	0.12	0.730	--	--	--	--	--	a	a
		Severity × Forest type	0.19	0.942							
	C (%)[b]	Severity	22.89	<**0.0001**	a	b*	b	b	b	--	--
		Forest type	0.21	0.650	--	--	--	--	--	a	a
		Severity × Forest type	0.63	0.644							
	N (%)	Severity	4.63	**0.007**	a	a	a	b	b	--	--
		Forest type	1.56	0.222	--	--	--	--	--	a	a
		Severity × Forest type	0.83	0.519							
	C:N ratio[c]	Severity	13.68	<**0.0001**	a	b	b	b	b	--	--
		Forest type	8.85	**0.006**	--	--	--	--	--	a	b
		Severity*Forest type	0.36	0.836							
	C (g m^{-2})[b]	Severity	3.68	0.024	a	b	b	b	a	--	--
		Forest type	0.05	0.833	--	--	--	--	--	a	a
		Severity*Forest type	0.08	0.989							
	N (g m^{-2})[b]	Severity	2.83	0.063	a	a	a	a	a	--	--
		Forest type	0.72	0.416	--	--	--	--	--	a	a
		Severity × Forest type	0.68	0.614							
0-10 cm	C (%)[b]	Severity	0.24	0.913	a	a	a	a	a	--	--
		Forest type	0.75	0.394	--	--	--	--	--	a	a
		Severity × Forest type	1.41	0.277							
	N (%)[c]	Severity	0.27	0.892	a	a	a	a	a	--	--
		Forest type	0.12	0.733	--	--	--	--	--	a	a
		Severity × Forest type	0.93	0.474							
	C:N ratio[c]	Severity	22.03	<**0.0001**	a	b	b	b	b	--	--
		Forest type	2.94	**0.093**	--	--	--	--	--	a*	b*
		Severity × Forest type	0.45	0.770							
	C (g m^{-2})[b]	Severity	0.71	0.596	a	a	a	a	a	--	--
		Forest type	0.5	0.489	--	--	--	--	--	a	a
		Severity × Forest type	1.91	0.165							
	N (g m^{-2})[b]	Severity	0.26	0.897	a	a	a	a	a	--	--
		Forest type	0.22	0.646	--	--	--	--	--	a	a
		Severity × Forest type	1.22	0.350							

[a]Bold text indicates statistical significance. Letters indicate significant differences among means at $p < 0.05$.
[b]Log transformed before analysis.
[c]Ranked before analysis.
*Differences significant at $p < 0.10$.

and Table 6). We also observed large increases in the percent contribution by proteins in the forest floor of both forest types and in the coniferous mineral soil, although there was no clear relationship with severity level. Coniferous forest floor lignin and lipid pools showed major losses in the lignin and lipid pools, whereas there were no clear effects in mineral soil. For deciduous forest floor and mineral soil, the greatest losses in lignin occurred in severity levels 1 and 2, whereas smaller losses occurred in severity level 4, relative to the control (Figure 2 and Table 6). Major increases in PyC pools occurred in the forest floor of both forest types, with differences of >60% and >33% between burned areas and the control for coniferous and deciduous sites, respectively (Figure 2 and Table 6). There was no clear pattern of response in coniferous mineral soil, and we surprisingly observed 0% PyC in the coniferous forest floor and mineral soil classified as severity 1. The PyC pool increased with severity in deciduous mineral soil (Figure 2 and Table 6). Burned forest floor layers were dominated by PyC, whereas the SOM in mineral soil had a more heterogeneous composition.

3.4. Fire Severity Effects on Proxies of SOM Stability and Decomposition

In coniferous forest, the lignin:N ratio decreased with severity in the forest floor and increased in the mineral soil in all severity levels (Figure 3). We observed a lesser increase of the stability index in deciduous mineral

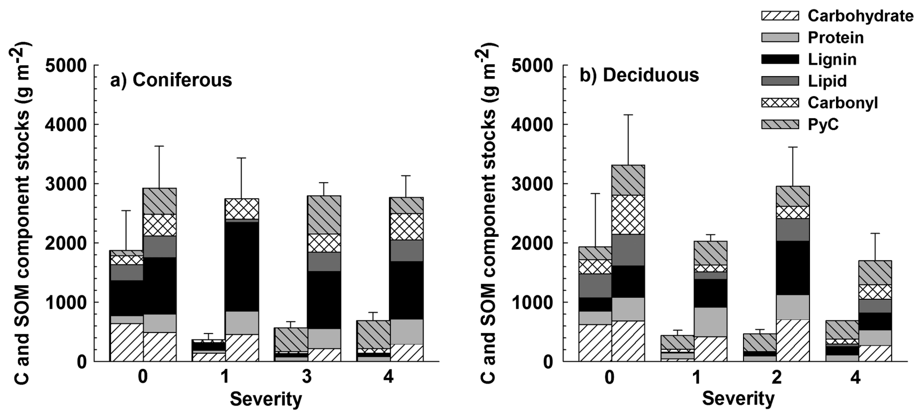

Figure 2. Soil organic matter component (SOM) stocks in the forest floor and mineral (0–10 cm) soil layers across a gradient of fire severity in (a) coniferous and (b) deciduous cover types. Shown are total mean (±SE) carbon stocks for all coniferous and deciduous areas sampled after the 2011 Pagami Creek wildfire in northern Minnesota, USA, and SOM stocks calculated from weight percent of observed carbon determined from ^{13}C NMR and a molecular mixing model. Forest floor layer data are shown in the left bar, and mineral soil data are shown in the right bar for each pair of bars within severity level.

soil, and no net change in the forest floor (Figure 3). The lignin:N ratios were consistently greater in coniferous forest than in deciduous forest.

The alkyl C:O-alkyl C ratio increased with severity in the coniferous forest floor, whereas in mineral soil only the high-severity area exhibited an increase in the ratio relative to the unburned control (Figure 3). Data from the deciduous forest floor show a lesser increase in the ratio, and there is no pattern evident in the mineral soil layer (Figure 3). Although the alkyl C:O-alkyl C ratio for unburned deciduous forest floor was nearly double the value for unburned coniferous forest floor, the magnitude of increase in the ratio across the severity gradient was greater in coniferous forest than in deciduous forest.

Table 6. Percent of SOC Contributed by SOM Components Determined by ^{13}C NMR and the Molecular Mixing Model for the Forest Floor Layer and 0–10 cm Mineral Soil Representing a Gradient of Fire Severity in Two Forest Cover Types[a]

			Percent of SOC (%)					
Cover Type	Horizon	Severity	Carbohydrate	Protein	Lignin	Lipid	Carbonyl	PyC
Coniferous	FF	0	34.2 (0.93)	6.9 (0.8)	31.5 (8.5)	14.6 (0.3)	8.1 (1.8)	4.6 (4.6)
		1	37.0	14.0	32.2	2.5	14.3	0.0
		2	--	--	--	--	--	--
		3	1.2 (1.2)	12.8 (1.1)	9.7 (3.0)	0.1 (0.1)	5.6 (2.1)	70.7 (2.9)
		4	0.0	12.0	8.1	0.0	11.4	68.4
	0–10	0	16.7 (2.4)	10.6 (0.2)	32.4 (6.1)	12.7 (2.9)	12.5 (4.3)	15.1 (6.9)
		1	16.5	14.5	54.3	2.2	12.4	0.0
		2	--	--	--	--	--	--
		3	6.1 (1.5)	14.2 (1.2)	29.2 (9.1)	7.6 (2.8)	12.9 (1.2)	30.1 (10.2)
		4	10.5	15.3	34.9	13.3	16.0	10.0
Deciduous	FF	0	32.2	11.8	11.5	20.8	12.4	11.3
		1	10.6	22.8	2.0	0.0	11.6	53.0
		2	0.0	20.7	11.9	1.2	1.8	64.4
		3	--	--	--	--	--	--
		4	0.0	16.5	19.3	7.1	12.2	44.9
	0–10	0	20.6	12.1	15.9	16.2	19.9	15.3
		1	20.6	24.7	22.9	6.3	5.7	19.8
		2	23.9	14.2	30.5	12.8	6.9	11.6
		3	--	--	--	--	--	--
		4	16.0	15.5	16.6	13.8	14.5	23.6

[a]All values are determined from DPMAS data, except we use CPMAS data for deciduous mineral soil severity 2 because of low signal to noise ratio in the DPMAS results.

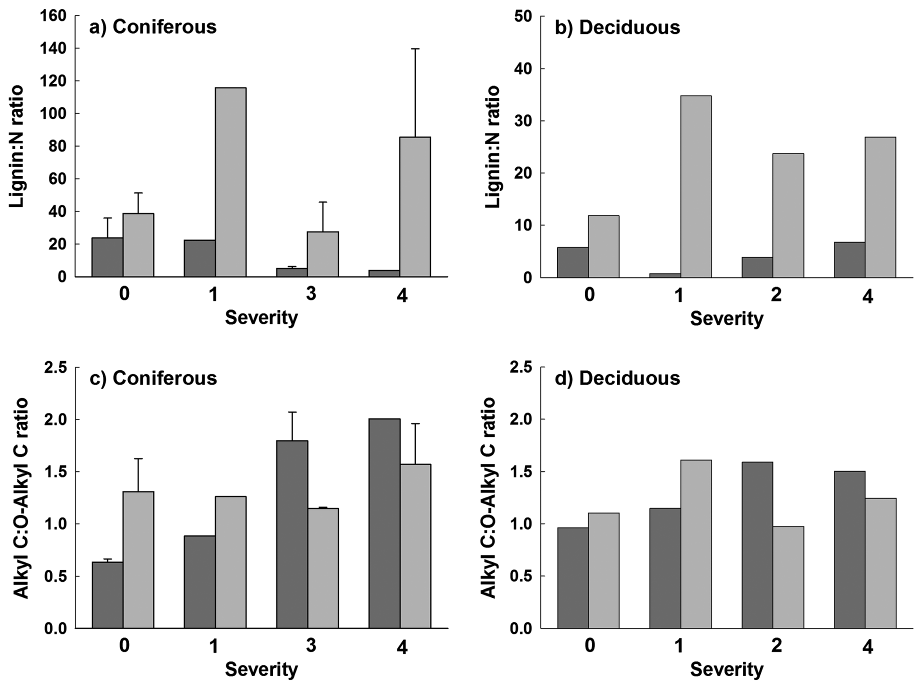

Figure 3. Ratios of (a, b) lignin to nitrogen and (c, d) alkyl carbon to O-alkyl carbon as proxies for soil organic matter quality for a gradient of fire severity in coniferous and deciduous forest cover types. Forest floor layer data are shown in the left (dark fill) bar, and mineral soil data are shown in the right (light fill) bar for each pair of bars within severity level. Note the difference in *y* axis scales between Figures 3a and 3b.

4. Discussion

Shifts in global and regional climate are likely to alter the range of fire combustion conditions relative to the range of historical conditions to which the forest is adapted. Our approach addressed the influences of forest type and fire severity on SOM composition in a fire-affected forest, using within-fire differences in fire severity as a proxy for anticipating effects of increased fire severity under future climate conditions. Although our study site was located in the southern boreal forest, the approach we used is transferrable across regions. Current understanding of the variability of fire effects within wildfires remains limited, yet it is critical for accurately understanding the factors that influence fire effects on ecosystem processes such as SOM turnover, C fluxes to the atmosphere, and C sequestration by recovering vegetation.

4.1. Fire Effects on Forest Floor and Mineral Soil C and N

We found that fire caused forest floor thickness, C concentration, and C stocks to decline, whereas there was no effect of fire on mineral soil C or N concentrations or stocks, across coniferous and deciduous forest cover types. These results agree with estimates from an earlier, broader evaluation at this study site that included a greater range of forest cover types [*Kolka et al*., 2014]. However, we observed a decrease in C:N ratios in forest floor and mineral soil layers in all severity levels even when there were no significant differences in C or N stocks. Lower C:N ratios suggest that fire affects SOM composition even when we do not detect effects on total C or total N alone. Oxidation (i.e., combustion) of SOM begins at 420°C and is preceded by a series of changes in SOM molecular characteristics that occur over progressively increasing temperature (i.e., dehydration, dehydrogenation, and decarboxylation of SOM prior to oxidation) [*Plante et al*., 2009]. Thus, SOM composition can undergo thermal reactions at temperatures well below 420°C even while the changes in total mass of soil C go undetected against the natural variation in soils.

Heckman et al. [2013] reported a narrowed C:N ratio that corresponded with increased mineral soil N concentrations across a fire severity gradient in an Oregon mixed conifer forest 2 years after the 2002 Biscuit fire, which they attributed to an increase in N availability due to N-fixing shrubs that colonized burned areas. In contrast, we conducted our sampling in late autumn, 1–2 months after the Pagami

Creek fire, and our results reflect changes in SOM composition that are not confounded by the response of new vegetation to fire severity. A laboratory investigation of fire severity on SOM in forest floor and upper mineral soil horizons also showed no impact on C concentrations in A horizons [*Hatten and Zabowski*, 2010]. The authors concluded that changes in mineral horizon SOM composition resulted from SOM transformations rather than combustion (i.e., loss) of C-containing compounds [*Hatten and Zabowski*, 2010].

4.2. Fire Effects on SOM Composition and PyC Pools

The mixing model results indicated that changes in SOM composition occur across the severity gradient. In the forest floor of both cover types, we observed a decrease in carbohydrate and lignin pools and an increase in the PyC (char) pool, and these patterns were more clear for coniferous forest than for deciduous forest. In the mineral soil, we observed a decrease in carbohydrate stocks, a possible decrease in the PyC pool, and no striking pattern in the lignin pool. Fires of all severity levels changed SOM composition away from carbohydrate compounds and toward dominance by PyC, although there is not always a direct relationship with severity level. Similarly, increased dominance by aromatic compounds in bulk mineral soil was also the most noticeable change in SOM reported from a study of 0–2.5 cm mineral soil from two fires described as moderately and extremely severe in central Italy and southeastern Australia, respectively [*Mastrolonardo et al*., 2015] and from 0–15 cm mineral soil after a high-intensity fire in a Spanish *Pinus pinaster* Aiton. forest [*Knicker et al*., 2005]. The relative contribution of the aromatic region in ^{13}C NMR spectra for mineral soil in both forest types in our study was similar in magnitude to the contributions reported by *Mastrolonardo et al*. [2015] for both sites, and by *Knicker et al*. [2005]. Changes in SOM composition in burned soils relative to unburned soils have been attributed in part to the disruption of soil aggregates by fire, via the release of lignin and polysaccharides from the occluded light fraction of mineral soil [*Mastrolonardo et al*., 2015].

The presence of "legacy char" in our unburned reference samples shows that past fires can confound interpretation of single-fire effects on PyC pools. Each new fire not only can produce PyC, it also can simultaneously consume legacy PyC—thus, we are not able to isolate a simple PyC presence/absence effect in a natural wildfire setting. Each fire is an overlay on past disturbances. In many cases, knowledge of the type and/or magnitude of past disturbance events is difficult to determine. Our study site is unique in that relatively detailed fire history records exist. However, the effect of fire on SOM can be confounded by vegetation composition (and therefore amount and composition of litter deposited to the soil surface and prefire SOM composition), as shown by the differences we observed between coniferous and deciduous forests. The difficulty in quantifying the specific effect of fire on SOM was also emphasized in a comparison of SOM composition in 0–10 cm mineral soil density fractions collected from sites with contrasting fire frequencies, confounded by differences in vegetation composition [*Mastrolonardo et al*., 2013]. Although the two forest cover types used in our study occurred at the same elevation, within the same soil type, experienced similar fire history, and were affected by the same wildfire event, PyC contributed a greater proportion of forest floor and 0–10 cm mineral soil C stock in coniferous forest than in deciduous forest in unburned and burned areas.

4.3. Implications of the Current Study for the C Cycle

As the scientific community continues to improve understanding of SOM—and especially PyC—dynamics, it will be important to place results into an ecosystem context. For example, PyC has been positively correlated with soil pH, total C and N, P availability, and conifer seedling regeneration [*MacKenzie et al*., 2008; *Makoto et al*., 2011], which suggests that the PyC component of SOM may play an important role in postfire forest recovery. In contrast, loss of the carbohydrate component may depress microbial activity after fire, at least until more labile compounds become incorporated into the soil via plant litter [*Gonzalez-Perez et al*., 2004]. Labile compounds facilitate microbial activity and can in fact result in increased mineralization of PyC, as shown by an incubation study of laboratory-produced char and microbial inoculum from burned soil, amended with glucose [*Nocentini et al*., 2010b]. Even in a controlled laboratory setting where litter inputs were excluded, the effects of laboratory-created fire severity on C mineralization were important in the short term but diminished over a 180 day incubation of mineral soil, whereas the response of the forest floor persisted [*Hatten and Zabowski*, 2009].

Relationships between the magnitude of fire impact on soil C and SOM composition may also differ among ecosystem types and can also be influenced by soil moisture condition and the extent of association between organic and mineral components of soil [*Plante et al*., 2009]. For example, fire in Mediterranean pine forest caused nearly complete removal of the organic (forest floor) horizon and changes in SOM composition that included an increase in the contribution of aromatic compounds, even though the impacts on mineral soil were minimal [*Certini et al*., 2011]. The ^{13}C NMR method we used provides a quantitative assessment of PyC for the forest floor layer and a conservative estimate for the upper mineral soil because we analyzed the <2 mm size fraction only.

4.4. Effects of Fire Severity and Associated Heating on SOM Composition

The decrease in the lignin:N ratio in the coniferous forest floor layer agrees with the narrowed C:N ratios and was driven primarily by losses in lignin pools rather than a gain in N. The coniferous mineral soil lignin:N ratios varied across the severity gradient and weakly suggested an increase in the stability index with severity. These ratios indicate much greater SOM stability in coniferous sites relative to deciduous sites. We used the ratio of alkyl C:O-alkyl C to indicate the relative extent of decomposition for SOM within forest type following *Baldock et al*. [1997], who showed that the chemical changes associated with the progression of decomposition in forest litter were related to an increase in alkyl C and a decrease in O-alkyl C when analyzed with ^{13}C NMR. Our results showed that the alkyl C:O-alkyl C ratios for the forest floor layers were greater for the two highest severity levels than for the low-severity areas or reference sites, for both forest types. Because all burned sites in our study were affected by the same fire event, our alkyl C:O-alkyl C ratios suggest that the forest floor in the moderate- and high-severity areas experienced a greater influence of heating relative to the low-severity areas and to the unburned reference sites. These alkyl C:O-alkyl C results also agree with our observed loss of carbohydrate stocks, which are associated with the O-alkyl C region of the NMR spectrum and are relatively thermally labile. For example, carbohydrate loss occurs between 300°C and 350°C, whereas the loss of aromatic compounds occurs between 400°C and 450°C [*Plante et al*., 2009]. Thus, the alkyl C:O-alkyl C ratios in our study sites reflect thermally facilitated decomposition, that is, changes in SOM composition due to heating during a fire event.

PyC formation occurs via thermal decomposition of organic matter in the absence of oxygen and begins at relatively low temperatures (i.e., 250°C) [*Baldock and Smernik*, 2002]. In contrast, the combustion of PyC occurs at relatively high temperatures compared to less condensed forms of organic matter, such as carbohydrates as mentioned above. Thus, there is a temperature threshold below which PyC could be produced during a fire but is not yet consumed unless the temperature of the fire exceeds the thermal stability of the PyC. This could explain the peak in total (forest floor + mineral soil) and mineral soil PyC stocks we observed in severity levels 2 and 3 (for deciduous and coniferous areas, respectively), relative to severity level 4. PyC created during a fire may not only contribute to decreased bioavailability of the charred material [*Baldock and Smernik*, 2002], it may also be less prone to thermal decomposition during subsequent fires than the more thermally labile components of SOM, unless subsequent fires generate relatively high temperatures (e.g., >400–450°C as discussed above) at the soil surface.

However, two recent reports provide evidence that a very low percentage of PyC is consumed in experimental fires, even at relatively high temperatures. For example, an experimental fire designed to mimic wildfire conditions in boreal jack pine forest in the Northwest Territories, Canada, resulted in a median mass loss of 6.6% for small PyC pieces (1.0–1.7 mm particle size) placed at approximately 2 cm depth into the forest floor layer, whereas there was a 15.1% median mass loss for individual pieces of 1.0–5.0 g each placed at the same depth [*Santin et al*., 2013]. The majority (75%) of the small particles and larger individual pieces lost <15% and <25% of their prefire mass, respectively, even though thermocouples placed at the forest floor surface registered maximum temperatures between 500°C and 976°C [*Santin et al*., 2013]. Similarly, experimental fire in open savanna woodlands in northern Australia resulted in <8% mass loss across a gradient of charcoal fragment size, and <2% of the total number of fragments studied were completely consumed during the fire even though maximum temperatures at 2 cm aboveground ranged between 600°C and 700°C [*Saiz et al*., 2014]. Together, data from these recent studies of macroscopic PyC fragments support the idea that PyC is largely resistant to combustion in subsequent fires.

4.5. Implications for Terrestrial to Aquatic Connections

Heterogeneity in prefire forest structure and wildfire conditions contributes to heterogeneity in postfire soil characteristics such as C stocks, SOM composition, and C dynamics. Although our study area lacks significant topographic variability that would contribute to major postfire erosion, it is located in an area that is heavily interspersed with a series of interconnected inland lakes and streams [*Heinselman*, 1996]. Recent evidence has shown that physical transport of fire-affected organic matter contributes a measureable proportion of dissolved organic matter to riverine systems [*Ding et al*., 2013; *Jaffé et al*., 2013; *Myers-Pigg et al*., 2015] and includes molecularly heterogeneous material such as relatively labile pyrogenic components with a half-life of $<$40 days [*Myers-Pigg et al*., 2015] as well as more chemically recalcitrant material [*Jaffé et al*., 2013]. Together, these studies show that the influence of fire on organic matter composition and dynamics extends across ecosystem boundaries and links terrestrial disturbance to carbon dynamics in aquatic and marine systems. Thus, differences in SOM composition and quality that exist across fire severity gradients indicate that shifts in fire regimes may also have implications for organic matter cycling in adjacent and downstream aquatic systems.

For example, *Myers-Pigg et al*. [2015] suggest that wildfires may increase C cycling in burned ecosystems as well as increase respiration rates within watersheds via the input of pyrogenic organic matter produced at relatively low temperatures (150–400°C), which is relatively more labile than organic matter produced at greater temperatures. PyC produced from fire in an oak shrubland shows a low level of aromatic condensation, and its influence on SOM quality does not persist much longer than a decade after fire [*Alexis et al*., 2012, 2010]. In contrast, we found that the PyC pool of the forest floor and upper mineral soil in our southern boreal forest contributed up to 15% of soil organic C in control areas that have not experienced fire since 1864. The persistence of the PyC signature in SOM composition at our study site suggests that the PyC produced during previous fire(s) (i.e., prior to the 2011 Pagami Creek fire) is retained on site as a large contributor to SOM in these forests. Greater temperatures of formation have been associated with greater PyC aromaticity and stability in the environment [*Alexis et al*., 2012, 2010; *Myers-Pigg et al*., 2015; *Wolf et al*., 2013]; however, it is important to note that particle size and the extent of physical protection in aggregates or microniches also influence the persistence of PyC and other forms of SOM in soil [*Nocentini et al*., 2010a; *Schmidt et al*., 2011].

Southern boreal forest, such as our focal ecosystem, supports varying combinations of surface fire and crown fire within a given wildfire. In this ecosystem as well as in forests that that experience similar fire dynamics, it is possible that pyrogenic organic matter transported through surface water may bear a different molecular signature over the short term following fire (indicating export of organic matter derived from surface fire) than the signature over the longer term as woody material charred during crown fire becomes incorporated into the forest soil via falling fire-killed trees. A shift toward increasingly high-severity fires therefore has the potential to alter short- and long-term organic matter composition and dynamics in terrestrial and aquatic to marine environments.

4.6. Caveats and Future Considerations

Our results agree with recent evidence that postfire organic material is a mixture of C pools with varying molecular composition. The greater variability in mineral soil SOM composition we observed across the severity gradients relative to forest floor SOM may reflect a diluted signal of fire because we sampled mineral soil to 10 cm depth. In general, mineral soils are poor conductors of heat, and soil heating to depths $>$5 cm is generally low unless the duration or temperature of heating is prolonged [*Neary et al*., 1999]. Assessing fire effects on mineral soils using the upper 5 cm increment may reveal clearer relationships between fire severity and soil characteristics in forest soil mineral horizons. However, we emphasize that the pattern in carbohydrate stocks emerged even when we used composited samples of the 0–10 cm mineral soil collected within a plot. The loss of the relatively easily accessible carbohydrate C and the increase in more stable PyC are likely to influence postfire SOM cycling and C flux over time as the forest recovers.

The response of some SOM characteristics followed the fire severity gradients whereas others did not. Severity estimated after a fire provides a metric for evaluating the overall magnitude of impact from fire—it is determined by (but does not provide retrospective information on) the temperature experienced during a fire, the intensity (rate of heat output) of a fire, and the duration of heating experienced at a given location [*DeBano et al*., 1998; *Jain et al*., 2012; *Neary et al*., 1999]. Data on combustion conditions during wildfires in natural settings will be important for efforts to connect aboveground processes—such as disturbance by fire—with belowground patterns—such as PyC pools and distribution, or postdisturbance SOM dynamics. Research on PyC is a relatively young field, as is the emerging paradigm on factors that drive SOM dynamics within and across ecosystems [*Marín-Spiotta et al*., 2014; *Schmidt et al*., 2011]. The variability in results among severity levels and among studies published to date highlights the need for additional work to understand relationships between ecosystem disturbances and SOM dynamics.

5. Conclusions

We have shown that wildfire in southern boreal forest contributes to changes in SOM composition and quality and that differences in patterns of SOM composition response to fire exist between forest cover types. The most pronounced effects occurred in the forest floor layer, which experiences more direct effects of fire than does the mineral soil. In the forest floor layer, we observed increases in PyC, a decreased index of SOM stability, and an increased index of decomposition with fire severity. These patterns appear to be driven by loss of the carbohydrate and lignin components and a gain of PyC in the forest floor layer. The responses of some SOM characteristics followed the fire severity gradient whereas others did not. The presence of PyC in forest floor and mineral soil layers in control plots that have not experienced fire for nearly 150 years suggests a persistent signal of potentially high-temperature PyC over the long term following fire. Our research provides intermediate-scale (plot-level) evaluation of relationships between fire severity and postfire SOM characteristics. Additional work is needed to determine the extent to which increases in future fire severity (and associated changes in combustion and pyrolysis conditions) will affect postfire biogeochemical cycling within and across forest types.

Acknowledgments
Data used for the results presented are available from the corresponding author upon request. Funding for this project was provided by NSF RAPID award 1201484 to Phil Townsend, Randall Kolka, and others, by an NSF EAR-IF 1132124 to Bill Hockaday, and by Michigan State University. We thank Sue Leitz for providing the fire location map, Charles Perry for providing prefire FIA data, the Townsend Lab and Superior National Forest personnel for field assistance, Nate Aspelin for lab assistance, Stephanie Grand for helpful discussion of the data, and Bernardo Maestrini and Lucas Michelotti for comments on the Discussion. All sampling was performed in compliance with agency guidelines and permitting requirements for research in federally designated wilderness areas. We thank two anonymous reviewers for their helpful comments on an earlier version of this manuscript.

References

Alexis, M. A., C. Rumpel, H. Knicker, J. Leifeld, D. Rasse, N. Pechot, G. Bardoux, and A. Mariotti (2010), Thermal alteration of organic matter during a shrubland fire: A field study, *Org. Geochem.*, *41*(7), 690–697.
Alexis, M. A., D. P. Rasse, H. Knicker, C. Anquetil, and C. Rumpel (2012), Evolution of soil organic matter after prescribed fire: A 20-year chronosequence, *Geoderma*, *189*, 98–107.
Baldock, J. A., and R. J. Smernik (2002), Chemical composition and bioavailability of thermally-altered *Pinus resinosa* (red pine) wood, *Org. Geochem.*, *33*(9), 1093–1109.
Baldock, J. A., J. M. Oades, P. N. Nelson, T. M. Skene, A. Golchin, and P. Clarke (1997), Assessing the extent of decomposition of natural organic materials using solid-state C-13 NMR spectroscopy, *Aust. J. Soil Res.*, *35*(5), 1061–1083.
Baldock, J. A., C. A. Masiello, Y. Gelinas, and J. I. Hedges (2004), Cycling and composition of organic matter in terrestrial and marine ecosystems, *Mar. Chem.*, *92*(1–4), 39–64.
Bond, W. J., and J. E. Keeley (2005), Fire as a global "herbivore": The ecology and evolution of flammable ecosystems, *Trends Ecol. Evol.*, *20*(7), 387–394.
Bond-Lamberty, B., S. D. Peckham, D. E. Ahl, and S. T. Gower (2007), Fire as the dominant driver of central Canadian boreal forest carbon balance, *Nature*, *450*(7166), 89–92.
Brown, D. J., W. H. Nowlin, E. Ozel, I. Mali, D. Episcopo, M. C. Jones, and M. R. J. Forstner (2014), Comparison of short term low, moderate, and high severity fire impacts to aquatic and terrestrial ecosystem components of a southern USA mixed pine/hardwood forest, *For. Ecol. Manage.*, *312*, 179–192.
Certini, G. (2005), Effects of fire on properties of forest soils: A review, *Oecologia*, *143*(1), 1–10.
Certini, G., C. Nocentini, H. Knicker, P. Arfaioli, and C. Rumpel (2011), Wildfire effects on soil organic matter quantity and quality in two fire-prone Mediterranean pine forests, *Geoderma*, *167–68*, 148–155.
de Groot, W. J., M. D. Flannigan, and A. S. Cantin (2013), Climate change impacts on future boreal fire regimes, *For. Ecol. Manage.*, *294*, 35–44.
DeBano, L. F., D. G. Neary, and P. F. Ffolliott (1998), *Fire's Effects on Ecosystems*, 333 pp., John Wiley, New York.
Deluca, T. H., and C. Boisvenue (2012), Boreal forest soil carbon: Distribution, function and modelling, *Forestry*, *85*(2), 161–184.
DeLuca, T. H., and G. H. Aplet (2008), Charcoal and carbon storage in forest soils of the Rocky Mountain West, *Front. Ecol. Environ.*, *6*(1), 18–24.
Ding, Y., Y. Yamashita, W. K. Dodds, and R. Jaffe (2013), Dissolved black carbon in grassland streams: Is there an effect of recent fire history?, *Chemosphere*, *90*(10), 2557–2562.
FIA (2011), *Phase 3 Field Guide—Soil Measurements and Sampling, Version 5.1*, 31 pp., USDA Forest Service, Forest Inventory & Analysis National Office, Arlington, Va.
FIA (2012), *Forest Inventory and Analysis National Core Field Guide, Volume I: Field Data Collection Procedures for Phase 2 Plots. Version 6.0*, 427 pp., USDA Forest Service, Forest Inventory & Analysis National Office, Arlington, Va.
Flannigan, M., B. Stocks, M. Turetsky, and M. Wotton (2009a), Impacts of climate change on fire activity and fire management in the circumboreal forest, *Global Change Biol.*, *15*(3), 549–560.
Flannigan, M., M. A. Krawchuk, W. J. de Groot, B. M. Wotton, and L. M. Gowman (2009b), Implications of changing climate for global wildland fire, *Int. J. Wildland Fire*, *18*(5), 483–507.
Flannigan, M., A. S. Cantin, W. J. de Groot, M. Wotton, A. Newbery, and L. M. Gowman (2013), Global wildland fire season severity in the 21st century, *For. Ecol. Manage.*, *294*, 54–61.
Franklin, J., A. D. Syphard, H. S. He, and D. J. Mladenoff (2005), Altered fire regimes affect landscape patterns of plant succession in the foothills and mountains of southern California, *Ecosystems*, *8*(8), 885–898.
Gelinas, Y., J. A. Baldock, and J. I. Hedges (2001), Demineralization of marine and freshwater sediments for CP/MAS C-13 NMR analysis, *Org. Geochem.*, *32*(5), 677–693.

Ghimire, B., C. A. Williams, G. J. Collatz, and M. Vanderhoof (2012), Fire-induced carbon emissions and regrowth uptake in western U.S. forests: Documenting variation across forest types, fire severity, and climate regions, *J. Geophys. Res.*, *117*, G03036, doi:10.1029/2011JG001935.

Gonzalez-Perez, J. A., F. J. Gonzalez-Vila, G. Almendros, and H. Knicker (2004), The effect of fire on soil organic matter—A review, *Environ. Int.*, *30*(6), 855–870.

Harris, D., W. R. Horwath, and C. van Kessel (2001), Acid fumigation of soils to remove carbonates prior to total organic carbon or carbon-13 isotopic analysis, *Soil Sci. Soc. Am. J.*, *65*(6), 1853–1856.

Hatten, J. A., and D. Zabowski (2009), Changes in soil organic matter pools and carbon mineralization as influenced by fire severity, *Soil Sci. Soc. Am. J.*, *73*(1), 262–273.

Hatten, J. A., and D. Zabowski (2010), Fire severity effects on soil organic matter from a ponderosa pine forest: A laboratory study, *Int. J. Wildland Fire*, *19*(5), 613–623.

Heckman, K., J. Campbell, H. Powers, B. Law, and C. Swanston (2013), The influence of fire on the radiocarbon signature and character of soil organic matter in the Siskiyou National Forest, Oregon, USA, *Fire Ecol.*, *9*(2), 40–56.

Heinselman, M. L. (1981), Fire and succession in the conifer forests of northern North America, in *Forest Succession: Concepts and Application*, edited by D. C. West, H. H. Shugart, and D. B. Botkin, pp. 374–405, Springer, New York.

Heinselman, M. L. (1996), *The Boundary Waters Wilderness Ecosystem*, 334 pp., Univ. of Minnesota Press, Minneapolis.

Hilli, S., S. Stark, S. Willfor, A. Smeds, M. Reunanen, and R. Hautajarvi (2012), What is the composition of AIR? Pyrolysis-GC-MS characterization of acid-insoluble residue from fresh litter and organic horizons under boreal forests in southern Finland, *Geoderma*, *179*, 63–72.

Homann, P. S., B. T. Bormann, R. L. Darbyshire, and B. A. Morrissette (2011), Forest soil carbon and nitrogen losses associated with wildfire and prescribed fire, *Soil Sci. Soc. Am. J.*, *75*(5), 1926–1934.

IPCC (2007), *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, 996 pp., Cambridge Univ. Press, Cambridge, U. K., and New York.

Jaffé, R., Y. Ding, J. Niggemann, A. V. Vähätalo, A. Stubbins, R. G. M. Spencer, J. Campbell, and T. Dittmar (2013), Global charcoal mobilization from soils via dissolution and riverine transport to the oceans, *Science*, *340*(6130), 345–347.

Jain, T. B., and R. T. Graham (2007), The relation between tree burn severity and forest structure in the Rocky Mountains, in *Restoring Fire-Adapted Ecosystems: Proceedings of the 2005 National Silviculture Workshop. Gen. Tech. Rep. PSW-GTR-203*, edited by R. F. Powers, pp. 213–250 , USDA Forest Service Pacific Southwest Research Station, Albany, Calif.

Jain, T. B., D. S. Pilliod, R. T. Graham, L. B. Lentile, and J. E. Sandquist (2012), Index for characterizing post-fire soil environments in temperate coniferous forests, *Forests*, *3*(3), 445–466.

Kane, E. S., W. C. Hockaday, M. R. Turetsky, C. A. Masiello, D. W. Valentine, B. P. Finney, and J. A. Baldock (2010), Topographic controls on black carbon accumulation in Alaskan black spruce forest soils: Implications for organic matter dynamics, *Biogeochemistry*, *100*(1–3), 39–56.

Kasin, I., and M. Ohlson (2013), An experimental study of charcoal degradation in a boreal forest, *Soil Biol. Biochem.*, *65*, 39–49.

Keeley, J. E. (2009), Fire intensity, fire severity and burn severity: A brief review and suggested usage, *Int. J. Wildland Fire*, *18*(1), 116–126.

Knicker, H. (2007), How does fire affect the nature and stability of soil organic nitrogen and carbon? A review, *Biogeochemistry*, *85*(1), 91–118.

Knicker, H., F. J. Gonzalez-Vila, O. Polvillo, J. A. Gonzalez, and G. Almendros (2005), Fire-induced transformation of C- and N-forms in different organic soil fractions from a Dystric Cambisol under a Mediterranean pine forest (*Pinus pinaster*), *Soil Biol. Biochem.*, *37*(4), 701–718.

Knicker, H., G. Almendros, F. J. Gonzalez-Vila, J. A. Gonzalez-Perez, and O. Polvillo (2006), Characteristic alterations of quantity and quality of soil organic matter caused by forest fires in continental Mediterranean ecosystems: A solid-state (13)C NMR study, *Eur. J. Soil Sci.*, *57*(4), 558–569.

Kolka, R., B. R. Sturtevant, P. Townsend, J. Miesel, P. Wolter, S. Fraver, and T. DeSutter (2014), Post-fire comparisons of forest floor and soil carbon, nitrogen and mercury pools with fire severity indices, *Soil Sci. Soc. Am. J.*, *78*(S1), S58–S65.

Leary, G. J., R. H. Newman, and K. R. Morgan (1986), A C-13 nuclear-magnetic-resonance study of chemical processes involved in the isolation of Klason lignin, *Holzforschung*, *40*(5), 267–272.

Lehmann, J., J. Gaunt, and M. Rondon (2006), Bio-char sequestration in terrestrial ecosystems—A review, *Mitigation. Adapt. Strategy Global Change*, *11*(2), 403–427.

Lehmann, J., J. Skjemstad, S. Sohi, J. Carter, M. Barson, P. Falloon, K. Coleman, P. Woodbury, and E. Krull (2008), Australian climate-carbon cycle feedback reduced by soil black carbon, *Nat. Geosci.*, *1*(12), 832–835.

Lehmann, J., M. C. Rillig, J. Thies, C. A. Masiello, W. C. Hockaday, and D. Crowley (2011), Biochar effects on soil biota—A review, *Soil Biol. Biochem.*, *43*(9), 1812–1836.

Liu, S. G., et al. (2011), Simulating the impacts of disturbances on forest carbon cycling in North America: Processes, data, models, and challenges, *J. Geophys. Res.*, *116*, G00K08, doi:10.1029/2010JG001585.

MacKenzie, M. D., E. J. B. McIntire, S. A. Quideau, and R. C. Graham (2008), Charcoal distribution affects carbon and nitrogen contents in forest soils of California, *Soil Sci. Soc. Am. J.*, *72*(6), 1774–1785.

Makoto, K., M. Hirobe, T. H. DeLuca, S. V. Bryanin, V. F. Procopchuk, and T. Koike (2011), Effects of fire-derived charcoal on soil properties and seedling regeneration in a recently burned *Larix gmelinii*/*Pinus sylvestris* forest, *J. Soils Sediments*, *11*(8), 1317–1322.

Marín-Spiotta, E., K. E. Gruley, J. Crawford, E. E. Atkinson, J. R. Miesel, S. Greene, C. Cardona-Correa, and R. G. M. Spencer (2014), Paradigm shifts in soil organic matter research affect interpretations of aquatic carbon cycling: Transcending disciplinary and ecosystem boundaries, *Biogeochemistry*, *117*(2–3), 279–297.

Masiello, C. A. (2004), New directions in black carbon organic geochemistry, *Mar. Chem.*, *92*(1–4), 201–213.

Mastrolonardo, G., G. Certini, R. Krebs, C. Forte, and M. Egli (2013), Effects of fire on soil organic matter quality along an altitudinal sequence on Mt Etna, Sicily, *Catena*, *110*, 133–145.

Mastrolonardo, G., C. Rumpel, C. Forte, S. H. Doerr, and G. Certini (2015), Abundance and composition of free and aggregate-occluded carbohydrates and lignin in two forest soils as affected by wildfires of different severity, *Geoderma*, *245*, 40–51.

Melillo, J. M., J. D. Aber, A. E. Linkins, A. Ricca, B. Fry, and K. J. Nadelhoffer (1989), Carbon and nitrogen dynamics along the decay continuum —Plant litter to soil organic-matter, *Plant Soil*, *115*(2), 189–198.

Miller, J. D., E. E. Knapp, C. H. Key, C. N. Skinner, C. J. Isbell, R. M. Creasy, and J. W. Sherlock (2009), Calibration and validation of the relative differenced normalized burn ratio (RdNBR) to three measures of fire severity in the Sierra Nevada and Klamath Mountains, California, USA, *Remote Sens. Environ.*, *113*(3), 645–656.

Muir, W. D. (1941), Forest fire control in the United States of America, The Forest History Society. [Available online at http://www.foresthistory.org/ASPNET/Policy/Fire/Suppression/Suppression.aspx, Accessed 22 April 2015.]

Myers-Pigg, A. N., P. Louchouarn, R. M. W. Amon, A. Prokushkin, K. B. Pierce, and A. Rubtsov (2015), Labile pyrogenic dissolved organic carbon in major Siberian Arctic rivers: Implications for wildfire-stream metabolic linkages, *Geophys. Res. Lett.*, *42*, 377–385, doi:10.1002/2014GL062762.

Neary, D. G., C. C. Klopatek, L. F. DeBano, and P. F. Ffolliott (1999), Fire effects on belowground sustainability: A review and synthesis, *For. Ecol. Manage.*, *122*(1–2), 51–71.
Nocentini, C., G. Certini, H. Knicker, O. Francioso, and C. Rumpel (2010a), Nature and reactivity of charcoal produced and added to soil during wildfire are particle-size dependent, *Org. Geochem.*, *41*(7), 682–689.
Nocentini, C., B. Guenet, E. Di Mattia, G. Certini, G. Bardoux, and C. Rumpel (2010b), Charcoal mineralisation potential of microbial inocula from burned and unburned forest soil with and without substrate addition, *Soil Biol. Biochem.*, *42*(9), 1472–1478.
Plante, A. F., J. M. Fernandez, and J. Leifeld (2009), Application of thermal analysis techniques in soil science, *Geoderma*, *153*(1–2), 1–10.
Preston, C. M. (2009), Biogeochemistry: Fire's black legacy, *Nat. Geosci.*, *2*, 674–675.
Preston, C. M., J. R. Nault, and J. A. Trofymow (2009), Chemical changes during 6 years of decomposition of 11 litters in some Canadian forest sites. Part 2 C-13 abundance, solid-state C-13 NMR spectroscopy and the meaning of "lignin", *Ecosystems*, *12*(7), 1078–1102.
Pyne, S. J. (1982), *Fire in America: A Cultural History of Wildland and Rural Fire*, Princeton Univ. Press, Princeton, N. J.
Rumpel, C., N. Rabia, S. Derenne, K. Quenea, K. Eusterhues, I. Kogel-Knabner, and A. Mariotti (2006), Alteration of soil organic matter following treatment with hydrofluoric acid (HF), *Org. Geochem.*, *37*(11), 1437–1451.
Saiz, G., L. Goodrick, C. M. Wurster, M. Zimmermann, P. N. Nelson, and M. I. Bird (2014), Charcoal re-combustion efficiency in tropical savannas, *Geoderma*, *219*, 40–45.
Santin, C., S. H. Doerr, C. Preston, and R. Bryant (2013), Consumption of residual pyrogenic carbon by wildfire, *Int. J. Wildland Fire*, *22*(8), 1072–1077.
Scheller, R. M., D. J. Mladenoff, R. C. Thomas, and T. A. Sickley (2005), Simulating the effects of fire reintroduction versus continued fire absence on forest composition and landscape structure in the Boundary Waters Canoe Area, northern Minnesota, USA, *Ecosystems*, *8*(4), 396–411.
Schmidt, M. W. I., et al. (2011), Persistence of soil organic matter as an ecosystem property, *Nature*, *478*, 49–56.
Smernik, R. J., and J. M. Oades (2000a), The use of spin counting for determining quantitation in solid state C-13 NMR spectra of natural organic matter 2 HF-treated soil fractions, *Geoderma*, *96*(3), 159–171.
Smernik, R. J., and J. M. Oades (2000b), The use of spin counting for determining quantitation in solid state C-13 NMR spectra of natural organic matter 1. Model systems and the effects of paramagnetic impurities, *Geoderma*, *96*(1–2), 101–129.
Smernik, R. J., and J. M. Oades (2001), Background signal in solid state C-13 NMR spectra of soil organic matter (SOM)—Quantification and minimization, *Solid State Nucl. Mag. Res.*, *20*(1–2), 74–84.
Todd-Brown, K. E. O., J. T. Randerson, W. M. Post, F. M. Hoffman, C. Tarnocai, E. A. G. Schuur, and S. D. Allison (2013), Causes of variation in soil carbon simulations from CMIP5 Earth system models and comparison with observations, *Biogeosciences*, *10*(3), 1717–1736.
Turner, M. G. (2010), Disturbance and landscape dynamics in a changing world, *Ecology*, *91*(10), 2833–2849.
van Bellen, S., M. Garneau, and Y. Bergeron (2010), Impact of climate change on forest fire severity and consequences for carbon stocks in boreal forest stands of Quebec, Canada: A synthesis, *Fire Ecol.*, *6*(3), 16–44.
Wolf, M., E. Lehndorff, G. L. B. Wiesenberg, M. Stockhausen, L. Schwark, and W. Amelung (2013), Towards reconstruction of past fire regimes from geochemical analysis of charcoal, *Org. Geochem.*, *55*, 11–21.
Wolter, P. T., and P. A. Townsend (2011), Multi-sensor data fusion for estimating forest species composition and abundance in northern Minnesota, *Remote Sens. Environ.*, *115*(2), 671–691.
Wolter, P. T., P. A. Townsend, and B. R. Sturtevant (2009), Estimation of forest structural parameters using 5 and 10 meter SPOT-5 satellite data, *Remote Sens. Environ.*, *113*(9), 2019–2036.
Woolf, D., and J. Lehmann (2012), Modelling the long-term response to positive and negative priming of soil organic carbon by black carbon, *Biogeochemistry*, *111*(1–3), 83–95.