

RESEARCH ARTICLE

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Key Points:

- Changes in soil BC over time indicate transport of BC during soil erosion
- Soil BC concentrations are inversely related to soil erosion and time since fire
- NMR techniques provide the most reliable way to determine soil BC

Supporting Information:

- Readme
- Text S1, Tables S1–S2, Figures S1–S2

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Changes in fire-derived soil black carbon storage in a subhumid woodland

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Abstract Fire-derived black carbon (BC) in soil, including charcoal, represents an important part in terrestrial carbon cycling due to its assumed long persistence in soil. Soil BC concentrations for a woodland in central Texas, USA, was found from study plots with a fire scar dendrochronology spanning 100 years. BC values were initially determined from ¹³C nuclear magnetic resonance (NMR) spectroscopy. The NMR-based BC concentrations were used to calibrate midinfrared vibrational spectra (MIRS) for evaluation as a less expensive and expedient technique. However, unexpectedly high BC values from the MIRS method were found for sites without evidence of fire for the past 100 years. Estimation of BC from NMR technique showed mean BC concentration of 2.73 ± 3.06 g BC kg⁻¹ (0.91 ± 0.51 kg BC m⁻²) for sites with fire occurrence within the last 40 years compared with BC values of 1.21 ± 1.70 g BC kg⁻¹ soil (0.18 ± 0.14 kg BC m⁻²) for sites with fire 40–100 years ago. Sites with no tree ring evidence of fire during the last 100 years had the lowest mean soil BC concentration of 0.05 ± 0.11 g BC kg⁻¹ (0.02 ± 0.03 kg BC m⁻²). Molecular proxies of stability (lignin/N) and decomposition (Alkyl C/O-Alkyl C) showed no differences across the sites, indicating low potential for BC mineralization. Modeled soil erosion and time since fire from fire scar data showed that soil BC concentrations were inversely correlated. These results suggest that the addition of BC may be limited by topography and timing of fire.

1. Introduction

Burning plant biomass produces an array of fire-derived compounds with polyaromatic and heterocyclic structures known as black carbon (BC). The current global sedimentary BC reservoir has been estimated to be 300–500 Gt C, composed of 5–30% of total organic carbon (TOC) from soil and freshwater inputs onto continental marine shelves [Hockaday et al., 2007; Lehmann et al., 2006; Masiello, 2004; Preston and Schmidt, 2006; Rodionov et al., 2010]. Fire affects terrestrial woodland ecosystem carbon cycles by consuming biomass and producing BC from incomplete combustion [Fuhlendorf et al., 1996; Chapin et al., 2002; Alexis et al., 2007]. Wildland fires are estimated to consume 4 to 8 Pg of terrestrial biomass C annually producing 0.5 to 1.7 Pg of BC [Reeves et al., 2008]. The large global pool size of BC highlights the importance of fire in terrestrial ecosystems; however, more information is needed to characterize residence time of terrestrial soil BC and mechanisms of terrestrial to marine flux rates.

Black carbon is broadly defined as chemically heterogeneous substances that include soot, charcoal, and slightly charred biomass. In the last decade, BC has gained attention as a substantial sink for sequestering atmospheric C due to the potential high residence time of BC in the soil which is estimated to be on the scale of hundreds to 10,000 years [Kuhlbusch and Crutzen, 1995; Lehmann et al., 2006; Liang et al., 2008]. The suggested longevity of BC in soils is due to the polyaromatic structure of compounds comprising BC that reduces biological decomposition [Forbes et al., 2006; MacKenzie et al., 2008]. Recent studies have found significant transportation and decomposition losses of BC from the soil at timescales of weeks to years that may indicate effective soil BC residence time on the order of hundreds of years [Alexis et al., 2012; Knicker et al., 2012; Singh et al., 2012].

Because BC is a continuum of organic compounds produced by fire [Hammes et al., 2007], a variety of analytical methods are required to measure it. Solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy can identify condensed aromatic C generally associated with pyrogenic BC in order to estimate concentrations in soil [Skjemstad et al., 1999; Simpson and Hatcher, 2004; Hockaday et al., 2007]. The advantage of ¹³C NMR spectroscopy is that it quantitatively determines the amount of organic C in different functional groups, such as Alkyl, O-Alkyl, aromatic, and phenolic, in a complex media such as soil [Smernik and Oades, 2000]. Because NMR

measurements are time intensive, there is a practical limit to the number of samples that can be analyzed. Alternatively, midinfrared spectroscopy (MIRS) may be used to predict various organic and inorganic soil properties based on statistical analysis of spectral absorption features [Janik and Skjemstad, 1995; Janik et al., 1995; Viscarra Rossel et al., 2006; Bornemann et al., 2008]. Therefore, MIRS can be used to detect aromatic C in order to estimate soil BC more rapidly than NMR [Colthup et al., 1990; Reeves et al., 2008]. However, MIRS can only be used for quantitative measurements when the method has been calibrated and corrected for matrix effects by using reference samples made from the soils-of-interest with known concentrations of the targeted compounds. Also, the similarity of the functional groups found in BC and the other nonpyrogenic materials, such as humic acids, may affect the quantitative accuracy of MIRS when these compounds are present in soil [Reeves et al., 2008].

To investigate the potential of soil BC as a long-term storage pool of terrestrial C, we assessed the concentration of wildland fire-derived soil BC from sites in a subhumid upland woodland for which the fire history was previously reconstructed using an extensive tree ring survey [Yao et al., 2012; Murray et al., 2013]. We measured the soil BC concentrations at these sites using NMR and MIRS techniques and compared to concentrations at sites with recent, old, and no documented fire occurrences. Decomposition of BC was assessed based on NMR-derived Alkyl C/O-Alkyl C values as a measure of the potential redox of the soil organic matter. To assess potential off-site transport, we modeled the potential soil erosion to compare with the best-estimate BC concentration values. Also, the legacy of burning on soil BC was analyzed by comparing time since last fire occurrence with soil BC concentrations. From these results, we proposed analytical contingencies and possible mechanisms important in assessing soil BC fluxes within a woodland ecosystem.

2. Study Area Description

Soil samples were collected from the woodlands of the Balcones Canyonlands National Wildlife Refuge (BCNWR), a 7109 ha U.S. federal land-holding located on the eastern edge of the Edwards Plateau, northwest of Austin, Texas, USA. Most fires over the past century in the refuge woodlands have been documented as having been nonstand replacing, low to moderate intensity surface fires [Yao et al., 2012]. These fires were suspected to have primarily consumed predominantly understory woody shrubs, tree seedlings and saplings, and infrequently mature trees. The refuge woodlands are dominated by evergreen Ashe's juniper (*Juniperus ashei*), and various broad-leafed hardwood species, such as Texas red oak (*Quercus buckleyi*), plateau live oak (*Quercus fusiformis*), scalybark oak (*Quercus sinuata* var. *breviloba*), post oak (*Quercus stellata*), and escarpment black cherry (*Prunus serotina* var. *eximia*) [Diamond, 1997; Gehlbach, 1988]. The refuge is climatically classified as subhumid, with mean annual precipitation of 855.0 mm, and mean annual minimum and maximum temperatures of 5.7°C to 16.8°C and 22.4°C to 33.5°C for winter and summer, respectively [National Climatic Data Center, 2011]. Soils are of the Brackett soil series taxonomically classified as loamy, carbonatic, thermic, shallow, typic Halustepts [U.S. Department of Agriculture, 1974].

3. Methods

3.1. Soil Sampling

To assess potential fire-derived BC, we collected two soil samples each from 60 plots that were established for a previous study [Yao et al., 2012]. These plots had only one recorded fire disturbance since the stand initiation and were separated by at least 300 m from other trees with recorded fire occurrence based on a tree ring study [Murray et al., 2013]. Each plot encompassed an 11.28 m radius circle for a total sampled area of 0.04 ha located on plateaus and hillsides with average slope about 15°. These plots were categorized into the three groups based on the time since last fire disturbance including: recent fire (<40 year), old fire (≥40 year), and no fire. Soil was collected below the litter layer 5 m from the plot center in the south and west directions from each plot and at least 1 m away from any standing trees to avoid obstruction by large roots. Using a soil auger with a 1.75 cm diameter, soil was sampled to a depth of 10 cm. The reduced depth of collection for these samples was due to sites being located both on plateau tops with very thin soils. The 10 cm depth was used as the standard for all sites to avoid bias. Rock fragments and biomass residuals were manually removed from soil samples before being dried at 60°C for 48 h in a gravity convection oven. From these samples, 5 g soil was ground to fine powder using a ceramic mortar and pestle. We then measured the soil BC concentration using the spectroscopic methods described below.

3.2. BC Detection Using ^{13}C NMR

Measuring BC in soils may be accomplished by direct detection of aromatic H and C from NMR; however, it requires extensive chemical preparation to reduce or eliminate confounding materials present in bulk soil samples. Indirect detection of BC may be accomplished utilizing MIRS as the chemical composition, and bond structure may provide a unique spectral signature across the infrared spectrum. Generally, MIRS is relatively simple and easy to sample numerous samples, although accuracy and precision are affected by calibration and concentration of BC in a soil sample

Because of the time required for solid-state ^{13}C NMR analyses, only a subset (18 samples) of the sample set (120 total, 2 samples for each plot) randomly selecting six soil samples from different plots of each fire group for analysis by NMR. To prepare for NMR analysis, we added approximately 3 g of the pulverized soil, referred to as w_1 , into 50 mL centrifuge tubes (VWR International LLC., Ultrahigh performance). We acidified these samples using 10 mL aqueous 10% HCl to volatilize inorganic carbon (i.e., carbonates), which was visually identified by effervescence [Harris *et al.*, 2001]. The HCl-treated soil suspension was then centrifuged at 8000 rpm for 10 min followed by aspiration of the supernatant. Samples were treated with fresh HCl every 2 h until no effervescence was visible. Because ^{13}C NMR spectra are adversely affected by high iron oxide concentration and low organic carbon concentration in soil [Gonçalves *et al.*, 2003], we further treated the soil samples with a mixture of 10% (w/w) hydrofluoric acid (HF) and 10% HCl (w/w). This procedure is intended to dissolve silicates and paramagnetic elements (Fe and Mn) while leaving the acid-insoluble organic matter, effectively, concentrating the organic C [Preston *et al.*, 1989; Schmidt *et al.*, 1997]. This was accomplished by adding 25 mL of 10% HF/HCl mixture in each tube, followed by sealing the tube and placing it horizontally on an oscillating table shaker for 12 h. Subsequently, samples were centrifuged at 8000 rpm for 10 min followed by careful aspiration of the supernatant. We repeated the HF/HCl acid treatment 3 times, rinsed the pellet with deionized water 3 times using the same procedure, dried in a gravity convection oven at 50°C for 48 h, and weighed for mass referred to as w_2 . The C and nitrogen (N) concentrations of the HF-treated soil samples were then determined by thermal combustion with an elemental analyzer (Thermo Flash 2000 series). The percent recovery rates of C after the HF treatment (C_R) were calculated as

$$C_R = \frac{C_{\text{HF}} \times \theta}{C_{\text{orig}}} \quad (1)$$

where C_{HF} is the percent organic C weight in the HF-treated soil, C_{orig} is the organic C weight percent in the untreated soil [Yao *et al.*, 2012], and θ is the percent of soil mass remaining after the HF treatment.

The solid-state ^{13}C NMR spectra of HF-treated soil samples were obtained using magic angle spinning techniques on a Bruker Avance III 300 MHz spectrometer operating at a ^{13}C resonance frequency of 75 MHz and using a Bruker double resonance probe. Approximately 250 to 300 mg pulverized soil was packed into a 7 mm diameter cylindrical zirconia rotor, sealed with a Kel-F end-cap and spun at 5 kHz. We collected NMR spectra using the cross polarization (CP) and the Bloch decay (BD) techniques, which were compared based on the mixing model prediction errors discussed later. The CP NMR spectra were acquired following a 90° ^1H excitation pulse, a 1 ms ^1H - ^{13}C contact pulse, and with a 5 s delay between acquisitions for 3000 scans. The chemical shift frequency was referenced to glycine as an external standard. Line broadenings of 30 Hz was applied prior to Fourier transformation. The BD (also known as single pulse and direct polarization) NMR spectra were acquired following a 90° ^{13}C excitation pulse with a 90 s delay between acquisitions for 800 scans. For the BD spectrum, the signal from the Kel-F rotor end-cap can significantly affect spectra [Smernik and Oades, 2000]; therefore, the end-cap spectrum was obtained as background and later subtracted from measured soil BD spectra.

Each spectrum (CP and BD) was phase and baseline corrected prior to integration. The spectra were first integrated between 0 and 220 ppm so that signals from all resonances were included for calculating the NMR detection of the ^{13}C nuclei in the sample (C_{obs}). The integrations of signal intensity were conducted by an adapted integration routine supplied with the instrument software (Topspin 3.0, Bruker Biospin). The C_{obs} was assessed by using glycine as standard, and assuming the C_{obs} of glycine was 100% [Smernik and Oades, 2000]. The C_{obs} was then determined for each sample as

$$C_{\text{obs}} = \frac{I_{\text{sample}} \times m_{\text{glycine}} \times C_{\text{glycine}}}{I_{\text{glycine}} \times m_{\text{sample}} \times C_{\text{sample}}} \quad (2)$$

where I is intensity determined from integration, m was the mass of the sample in the NMR rotor, and C was the percentage C concentration for either the sample of glycine. *Smernik and Oades* [2003] showed that CP NMR intensity of HF-treated soils is often underestimated by the above equation because the magnetization intensity (I_{sample}) relaxes more rapidly than I_{glycine} during the 1 ms contact time, via a process known as $T_{1\rho}^{\text{H}}$ relaxation. No attempt was made to correct CP NMR spectral intensities for the difference in $T_{1\rho}^{\text{H}}$ relaxation. Therefore, our spin counting of the CP NMR spectra provide a conservative measure of C_{obs} .

The spectra were then integrated for seven major functional groups associated with chemical shift regions: Alkyl C (0 to 45 ppm), N-Alkyl/Methoxyl C (45–60 ppm), O-Alkyl C (60 to 95 ppm), Di-O-Alkyl C (95 to 110 ppm), aromatic C (110 to 145 ppm), phenolic C (145 to 165 ppm), and carbonyl C (160 to 215 ppm) [*Knicker and Lüdemann*, 1995]. These integration results, along with C and N concentrations, were used as inputs into a molecular mixing model to estimate the concentrations of four classes of biopolymer (including carbohydrates, proteins, lignin, and lipids) as well as charcoal and carbonyl C [*Nelson et al.*, 1999; *Baldock et al.*, 2004; *Nelson and Baldock*, 2005]. Assignments of ^{13}C NMR signal intensity in the chemical shift regions associated with each biomolecule component of the molecular mixing model and their molar elemental concentrations normalized to C concentration were derived from parameters of a previous study using standard references materials of each component to parameterize the mixing model for soil ecosystems [*Baldock et al.*, 2004]. The predicted proportions of each biomolecule component calculated by the model are expressed on a TOC basis (%). These values were then adjusted according to the mass loss during the acid treatment to calculate biomolecular concentrations in untreated soil (g BC kg^{-1} soil). For example, the BC concentration in untreated soil can be calculated as

$$\text{BC} = 10 \times f \times C_{\text{HF}} \times (w_1/w_2) \quad (3)$$

where f is the BC/TOC ratio as a percentage, C_{HF} is the percentage of C concentration in HF-treated soil determined by elemental analyzer, w_1 is the weight of soil before treatment, and w_2 is the weight of soil after HF acid treatment. We referred to the results of the molecular mixing model using CP and BD NMR data as CP NMR + and BD NMR + models, respectively.

To confirm detectability of BC in soil using the NMR method, we obtained a laboratory-produced BC standard derived from chestnut wood with $682.0 \text{ g C kg}^{-1}$ and 1.6 g N kg^{-1} [*Hammes et al.*, 2006] that we added to a sample soil from a site without known evidence of fire (in the tree ring record or historical record) to produce a 14% wt/wt BC/soil mixture that was also subjected to the HF/HCl treatment. The CP and BD NMR spectra were then obtained and compared for the BC-free soil, pure BC, and soil BC mixture. To assess the soil organic matter (SOM) decomposition extent in these samples, we used a NMR-based proxy that derived from the ratio of NMR spectra peak areas Alkyl C/O-Alkyl C. The ratio increases with decomposition [*Baldock et al.*, 1997] which we calculated for samples analyzed by the NMR method. Alkyl C is related to the original input of recalcitrant compounds such as wax or cutin from plant material while O-Alkyl C is a metabolic product from microbial decomposition of bioavailable carbohydrates.

Estimated BC derived from these methods were converted from soil concentrations (g BC kg soil^{-1}) to mass density values (kg BC m^{-2}). This was accomplished using data and methods described in *Yao et al.* [2012] using top of the soil BC concentration, bulk density, and modeled soil depth, with assumed variable C content with soil depth.

3.3. BC Detection Using MIRS

All pulverized soil samples (120 samples, 2 samples for each plot, including 18 plot samples used for the NMR analysis) were scanned in a Thermo Scientific Nicolet 380 Fourier transform infrared spectrometer (Thermo Electron Scientific Instruments LLC, Madison, WI, USA) equipped with a “Smart Performer” attenuated total reflectance accessory (model 0039–555) with proprietary Germanium on KBr beam splitter and a deuterated glycine trisulfate detector. Each sample was scanned in the wave numbers range of 4000 to 400 cm^{-1} (i.e., wavelengths range from 2500 to $25,000 \text{ nm}$) at 4 cm^{-1} resolution for 32 scans to produce one spectrum and using Helium Neon as reference laser. Two repeated scans were conducted for each soil sample under the constant flow of N_2 gas through the spectrometer, and measurements were automatically corrected for water vapor and atmospheric CO_2 .

To account for measurement variations of diffuse reflectance spectroscopy of pulverized soil samples [*Janik et al.*, 1998], spectra were applied with appropriate treatments before comparison, including baseline correction and mean standardization. Baseline corrections were completed using the instrument software

(EZ OMNIC 7.3, Thermo Electron Corporation) to correct for uneven baselines. Spectra were then mean centered using the spectral regions that correspond to the most invariable zone (1861 to 2561 cm^{-1} in this study) where the standard deviation values were close to or equal to zero as the reference zone for standardization [Cadet and Offmann, 1996].

To estimate soil biomolecule concentrations, we used partial least squares regression (PLSR) analysis of MIRS absorption data. Biomolecule concentration data estimated by the NMR analysis were first transformed by calculating the square root of the data before entry into the PLSR model to minimize nonlinearity in the calibration [Janik *et al.*, 2007]. The calibration of the PLSR was completed by combining the square roots of biomolecule concentrations estimated by the NMR + model method from the 18 soil samples (six for each fire group) with the MIRS absorption spectra, followed by transformation into a smaller set of orthogonal PLS loadings with derived scaling terms [Haaland and Thomas, 1988; Janik *et al.*, 2007]. Best fit calibration models were developed using the one-out cross-validation procedure [Efron, 2004]. Although PLSR is a full spectrum method, from our preliminary analysis, we found that removal of certain spectral ranges enhanced the accuracy of the PLSR models. The optimal spectral range to use in the final PLSR calibration was selected to be 4000–1030 cm^{-1} based on the root-mean-square error of prediction (RMSEP) and the coefficient of determination (R^2) between measured and predicted values [Geladi and Kowalski, 1986]. After calibration, the PLSR model was used to predict the square roots of biomolecule concentrations for the remaining 42 samples (14 for each fire group). Calibration and prediction of the PLSR model were performed for the six biomolecule concentrations (R, version 2.13.1, The R Foundation for Statistical Computing). The results predicted from the PLSR model were squared to obtain the predicted biomolecule concentrations values, and results of two soil samples from each plot were then averaged to calculate plot means.

Differences in concentration of the six biopolymer concentrations between three fire groups were assessed for estimated values from both the NMR + model methods and the MIRS method using an analysis of variance (ANOVA) (Statistical Package for the Social Sciences 20) [Stroup and Stubbendieck, 1983; McCune and Grace, 2002]. The independent Student's *t* test was used to assess differences in the measured biopolymer component concentrations between any two fire groups. Significance level was set a priori at 0.05.

From these results, we calculated the lignin/N for all 120 samples as a proxy for SOM stability as this ratio has been shown to increase with lower rates of SOM turnover [Melillo *et al.*, 1989]. Lignin was predicted by MIRS study and N% data were derived from combustion elemental analysis from a previous study [Yao *et al.*, 2012].

3.4. Soil Erosion Modeling, Disturbance, and BC Transport Loss

To assess potential BC off-site transport due to soil erosion, we investigated the relationship between the soil erosion at sampled locations and the soil BC concentrations estimated from the CP NMR + and BD NMR + models. Only plots with detected BC from these methods were used. We used the NMR-derived BC estimates because the NMR method represented the most direct and potentially best estimates of soil BC concentrations.

Soil erosion was modeled at each plot using the Revised Universal Soil Loss Equation (RUSLE) [Renard and Freimund, 1994]. In this model, upslope soil erosion (A , $\text{t ha}^{-1} \text{yr}^{-1}$) is the product of six factors including: R representing rainfall-runoff erosivity [$(\text{MJ mm}) (\text{ha h/yr})^{-1}$], K representing soil erodibility factor [$(\text{t ha h}) (\text{ha MJ mm})^{-1}$], L representing upslope drainage length, S representing topographic slope steepness in degrees, C representing cover management, and P representing conservation support practice. The values of L , S , C , and P are all dimensionless. Because of the small area of analysis, the value of R was kept constant with a value of 4425 $(\text{MJ mm}) (\text{ha h/yr})^{-1}$. This value was derived from Renard *et al.* [1997] for the BCNWR. A constant value of 0.37 was used for C derived from Kouli *et al.* [2009] representing a transitional woodland. A value of 1.0 was used for P indicating no on-site effort to preserve soil at the BCNWR which is consistent with the current management practices there. To estimate soil erodibility, K , we first downloaded the digital Soil Survey Geographic (SSURGO) shape files for Burnet, Travis, and Williamson counties which include the BCNWR from the Natural Resources Conservation Service (<http://soils.usda.gov/survey/geography/ssurgo/>). For each plot, the surface soil value of K was extracted from the accompanying SSURGO database for the soil type presented at each plot. For L and S , we acquired a National Elevation Data (NED) with 10 m resolution for the BCNWR derived from the U.S. Geological Survey (<http://nationalmap.gov/viewer.html>). Using image processing software (ERDAS, Imagine 11.0, Intergraph, Madison, AL), we derived topographic slope (β) in degrees using a topographic analysis algorithm present in the software. For slope length (λ), plot locations

Table 1. Soil Chemistry by Fire Group^a

	C _{pre-HF} (g kg ⁻¹)	N _{pre-HF} (g kg ⁻¹)	Mass Loss (%)	C _{post-HF} (g kg ⁻¹)	N _{post-HF} (g kg ⁻¹)	Alkyl C/O-Alkyl C (CP)	Alkyl C/O-Alkyl C (BD)
Recent	78.43 (18.71)	5.41 (1.42)	83.48 (3.63)	430.52 (62.64)	29.44 (5.94)	0.98 (0.13)	1.01 (0.14)
Old	73.82 (26.45)	5.05 (1.67)	83.19 (6.84)	406.57 (38.93)	29.37 (3.21)	0.98 (0.07)	0.99 (0.07)
No	81.28 (24.35)	5.47 (1.43)	84.59 (5.10)	442.95 (52.91)	28.08 (1.84)	1.01 (0.11)	1.11 (0.12)

^aMean and standard deviations of the soil chemical characteristics of samples soil before and after the HF treatment with associated mass loss for each fire group. The Alkyl C/O-Alkyl C ratios derived from the NMR data are an indicator of SOM decomposition extent. The age of recent fires is <40 years and old fires ≥40 years.

were first visualized overlain on the NED in gray scale color. Using a measuring tool available with the image processing software, a line from the plot to the upslope point at the top of the drainage visually interpreted as the top of the drainage was digitized with the linear distance of λ provided in meters. The value of λ was converted into feet then used in the calculation of the product of S and L (SL) for each plot by

$$SL = (\lambda/72.6)^m (65.41 \sin^2\beta + 4.56 \sin\beta + 0.065) \quad (4)$$

where m is a derived coefficient whose value is determined based on β [Wischmeier and Smith, 1978].

All six factors were input into RUSLE to calculate the final values of A . These values were compared plot values of soil BC obtained from the CP NMR+ and BD NMR+ models. In addition, nonpyrogenic soil carbon was also estimated based on the total organic carbon measured for each sample minus BC. Nonpyrogenic soil organic carbon (SOC) was also compared to RUSLE-estimated soil erosion to assess potential preferential loss of BC from the system. Finally, soil BC estimates and nonpyrogenic SOC were compared with time since last fire (in years) to assess the legacy of fire disturbance as a driving variable for soil BC.

4. Results

4.1. BC Estimated by ¹³C NMR

For the 18 HF/HCl-treated soil samples prepared for the NMR analysis, the average soil mass loss due to the removal of carbonates, iron oxides, and silicates by acid treatment was $83.8 \pm 5.3\%$ (one standard deviation). After the HF/HCl treatment, the soil C and N concentrations increased compared to the values before the HF/HCl treatment, with no significant differences found between different fire groups (Table 1). The recovery of C following the demineralization procedure was $84.7 \pm 12.8\%$. The BC concentration predicted by the CP NMR+ model method for the recent fire group was higher than the value of the old fire and no fire group based on the independent Student's t test ($p = 0.005$). The BC concentration predicted by the BD NMR+ model method for the recent fire group was also higher than the value of the old fire group, and the value of old fire group was significantly higher than the value of the no fire group ($p = 0.038$). The BC concentration predicted by the BD NMR+ model method (average 1.40 ± 2.64 g C kg⁻¹ soil for all 18 samples) were higher, but not significantly, than the values predicted by the CP NMR+ model method (average 0.87 ± 1.41 g C kg⁻¹ soil). The mixing model predictions based on the BD NMR spectra had higher model and precision (4.32 ± 4.3), indicated by the sum of square error, than the model predictions based on the CP NMR spectra (10.07 ± 5.78).

To better evaluate the quantitative reliability of the NMR spectroscopy, we performed spin counting experiments for all samples. The spin counting results indicate that the C observability (C_{obs}) in the demineralized samples was $62.9 \pm 3.9\%$ for the CP NMR and $100 \pm 10\%$ for the BD NMR with no significant differences between fire groups. The relatively low C_{obs} of CP NMR indicates that it is possible for some SOM components to be underestimated in the CP NMR+ model results. To more directly assess the observability of BC by NMR, we used a chestnut wood BC standard mixed with soil at a rate of 14 wt % C. The NMR spectra showed a clear increase in aromatic C (110 to 145 ppm) with the addition of 14 wt % BC, which demonstrated the ability of NMR technique to detect the added BC. The soil BC mixture had a BC content of 69 g BC kg⁻¹ ($14\% \text{ BC} \cdot 493$ g C kg⁻¹ = 69 g BC kg⁻¹). Our analysis of the BC/soil mixture indicated a 30 g C kg⁻¹ of soil BC content by the CP NMR+ model and 57 g C kg⁻¹ by the BD NMR+ model. Therefore, the BC detection efficiency was 44% for CP NMR and 83% for BD NMR ($30/69 = 44\%$ and $57/69 = 82.6\%$). Therefore, the low C_{obs} values for CP NMR can be (at least partially) attributed to the underestimation of BC, whereas the BC detection efficiency for BD NMR analysis of the bulk SOM were similar to that of the BC standard (within measurement uncertainty), indicating that BD NMR+ model does not preferentially underestimate BC.

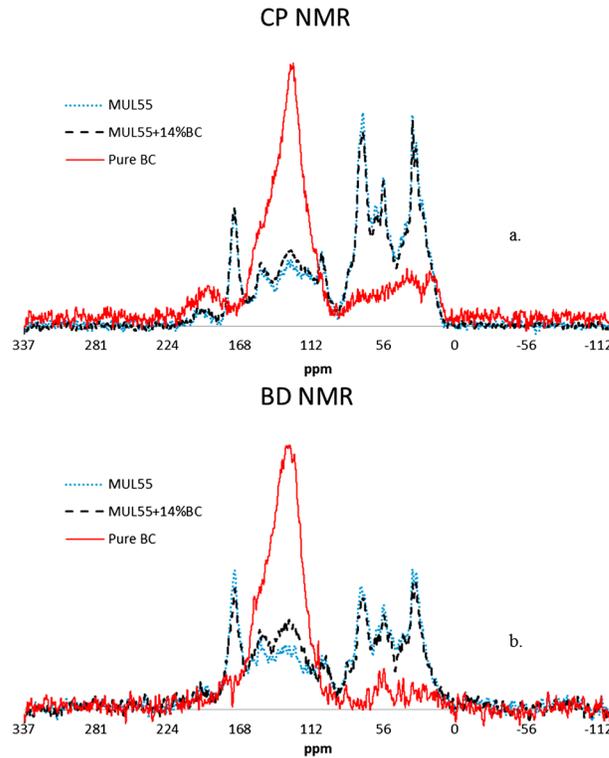


Figure 1. The (a) CP and (b) BD NMR spectra of BC-free soil (from the plot MUL55), mixture of soil and 14 wt % chestnut wood BC standard (labeled as: MUL55 + 14% BC), and pure chestnut wood BC standard are shown. The major chemical shift region for aromatic C is from 110 to 145 ppm. All spectra were scaled to equal magnitude upon integration from 0 to 220 ppm.

with no significant differences between fire groups (Table 1). There were also no significant differences found in the estimated biomolecule concentrations among the three fire groups based on ANOVA analysis.

4.3. BC Estimated by MIRS

The derived eight components PLSR calibration model showed very high correlation of MIRS and the BD NMR + model predicted values for BC, protein, lignin, and lipid indicated by low RMSEP and high R^2 values. The PLSR calibration correlation slightly decreased for carbohydrate and carbonyl (Figure 3). The average values

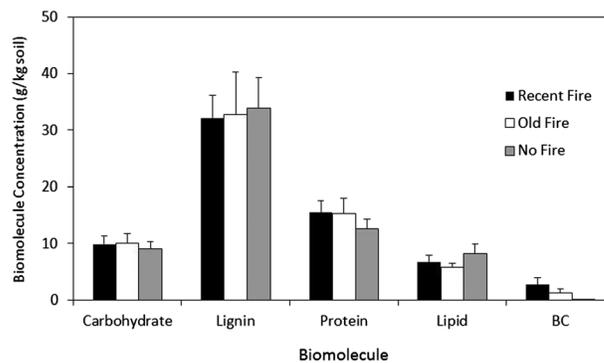


Figure 2. The estimated concentrations of the six biomolecules from the three fire groups predicted by the BD NMR + model method. Bars represent one standard deviation from the mean for each fire group ($n = 6$). The age of recent fires is <40 years and old fires ≥ 40 years.

of biomolecule concentrations predicted by the MIRS methods were similar to the results of the NMR + model methods (Table S1). We found significant differences of the BC concentrations between the recent fire group (sites with recent fire occurrences) and the old fire group (sites with older fire occurrences) ($p < 0.005$). No significant differences of any other biomolecule concentration values were found between the fire groups.

4.2. ^{13}C NMR Analysis of the Non-BC Components of SOM

The CP and BD NMR spectra both showed that SOM was dominated by organic matter with chemical shift regions associated with Alkyl C (0 to 45 ppm), O-Alkyl C (60 to 95 ppm), and amide/carboxyl C (160 to 215 ppm) groups (Figure 1). Based on the NMR + model, the dominant biomolecule components of the SOM were lignin, protein, and carbohydrate (Figure 2 and Table S1 in the supporting information). We also estimated the average SOM decomposition proxy, the Alkyl C/O-Alkyl C ratio 1.03 ± 0.12 from the BD NMR data

Due to the higher precision of estimating BC based on the fit of the mixing model (lower sum of square error) of the BD NMR data, we used the BD NMR + model predicted soil biomolecule concentrations to calibrate the PLSR of MIRS. Of the original 18 samples, only 15 had detectable BC from the BD NMR + model. These 15 BD NMR + BC estimates are used for the remainder of our analysis and discussion of NMR and BC in the ecosystem. The time since fire based on the fire scar data and results of CP NMR results can be found in the supporting information.

We found that the BC concentrations predicted by the MIRS method were higher than the results predicted by the NMR + model methods, especially significant for the no fire group ($p < 0.001$). Because of the high values predicted for

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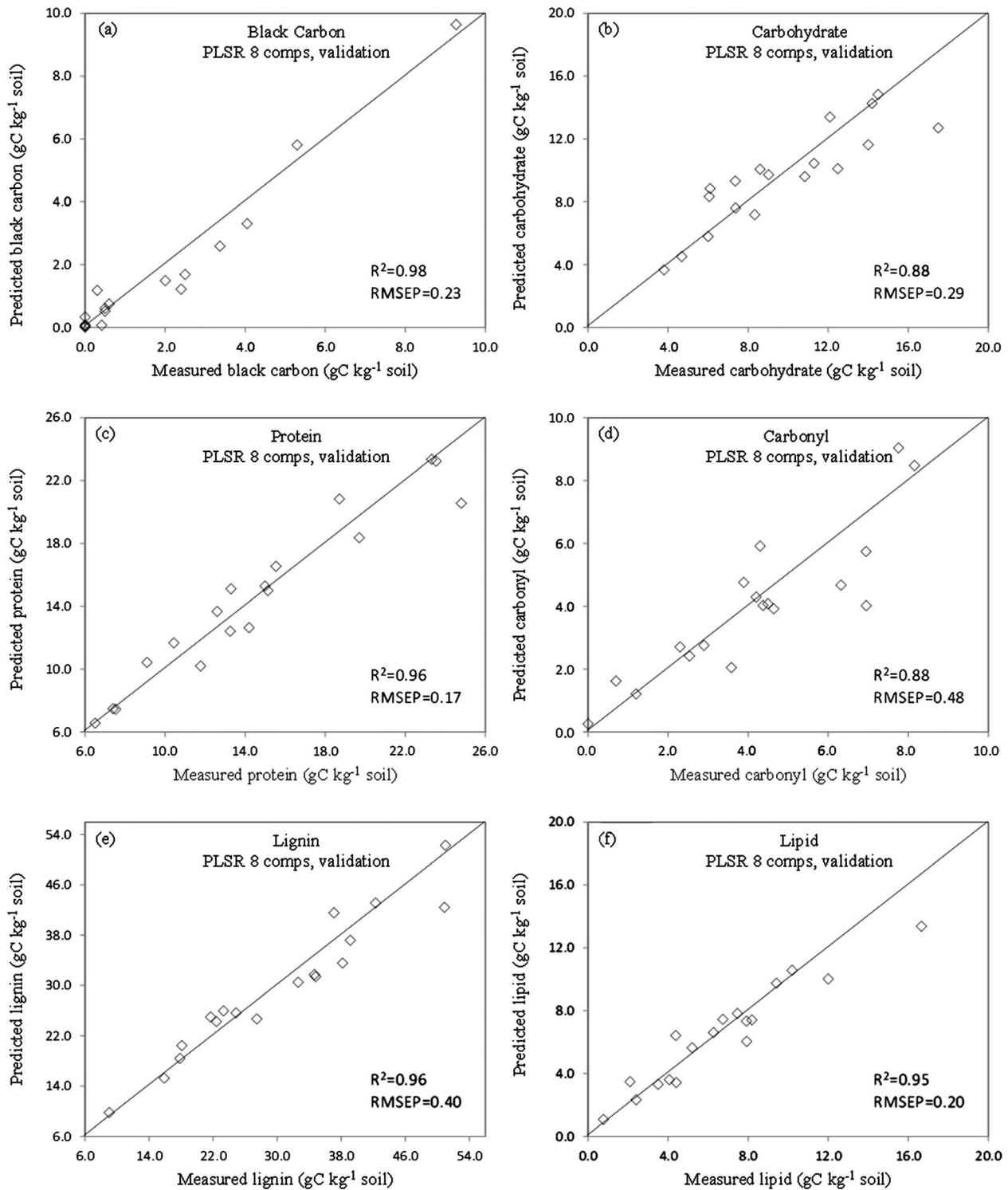


Figure 3. The plots of MIRS-predicted versus NMR + determined values from a leave-one-out cross validation of PLSR model for (a) black carbon, (b) carbohydrate, (c) protein, (d) carbonyl, (e) lignin, and (f) lipid. The results were transformed to concentration values (g C kg⁻¹ soil) by taking the square of the predicted values for each constituent as the PLSR were developed for the square roots of the measured biomolecule concentrations.

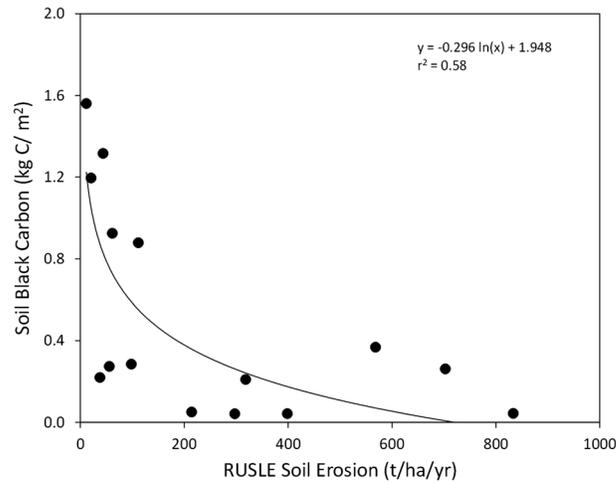


Figure 4. The relationship between soil erosion loss on an annual basis from the RUSLE model in $\text{ton ha}^{-1} \text{yr}^{-1}$ and soil black carbon (kg C m^{-2}) from the BD NMR + model. The results of a least squares regression based on a log-linear relationship with regression and coefficient of determination values are presented.

Mean annual soil erosion, A , predicted from these data was $176.3 \text{ metric ton ha}^{-1} \text{yr}^{-1}$. The range of time since fire for these samples based on the fire scar dendrochronology was 5 to 98 years (referenced to 2008). Multiplication of these year values by plot specific A values produced a mean, cumulative soil erosion since fire of $6435.8 \text{ metric ton ha}^{-1}$.

An inverse log-linear relationship was found between soil erosion loss on an annual basis from the RUSLE model and soil BC values estimated from the BD NMR + model (Figure 4). The coefficient of determination (r^2) for the regression was moderate with a value of 0.58. When compared with time since fire, a similar inverse log-linear relationship with soil BC was found with $r^2 = 0.57$ (Figure 5). We found a positive, linear relationship between RUSLE model and nonpyrogenic SOC values, which was moderately correlated with high variance ($r^2 = 0.57$; Figure 6). No correlation was found between time since fire and nonpyrogenic SOC.

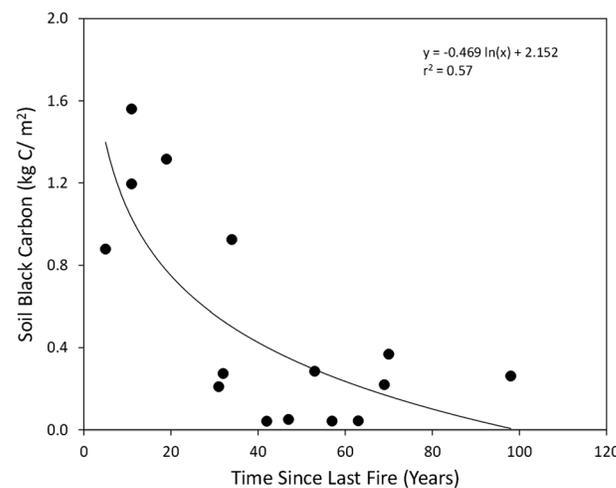


Figure 5. The relationship between time since last fire (years) derived from the fire scar data and soil black carbon (kg C m^{-2}) from the BD NMR + model. The results of a least squares regression based on a log-linear relationship with regression and coefficient of determination values are presented.

the no fire group, the MIRS BC concentrations were not analyzed for soil erosion and disturbance effects. For SOM stability analysis, the average lignin/N ratio was estimated to be 4.84 ± 1.46 , 6.85 ± 2.40 , and 5.26 ± 1.63 for the recent, old, and no fire group, respectively, with no significant difference between fire groups.

4.4. Soil Erosion and Time Since Fire Comparison

Using the geographical data, the mean K value for the plots was $0.042 \text{ (t ha h) (ha MJ mm)}^{-1}$ that ranged from 0.039 to $0.0481 \text{ (t ha h) (ha MJ mm)}^{-1}$. The mean value of β was 7.0° for the NMR analyzed plots was less than the 15.3° for the total 60 plots. The mean value of λ was 80.1 m with a range of 24.1 to 311 indicative of our sampling across a distribution of topographic positions. The mean calculated SL value was 3.18 .

5. Discussion

5.1. Factors Related to MIRS-Predicted BC

MIRS was used to estimate soil BC and was potentially advantageous compared to NMR because of the relatively inexpensive and fast results obtained from this technique. Large numbers of samples may be measured where MIRS produces robust results. However, we found the MIRS to estimate suspect BC values, such as the significantly high amounts of BC for sites without evidence of fire for the past century. This limited reliability of use for assessing the relationships of soil BC with landscape patterns including soil erosion and fire. For our study, several confounding factors affected this result.

The MIRS method is theoretically based on light absorption by vibrations of covalent

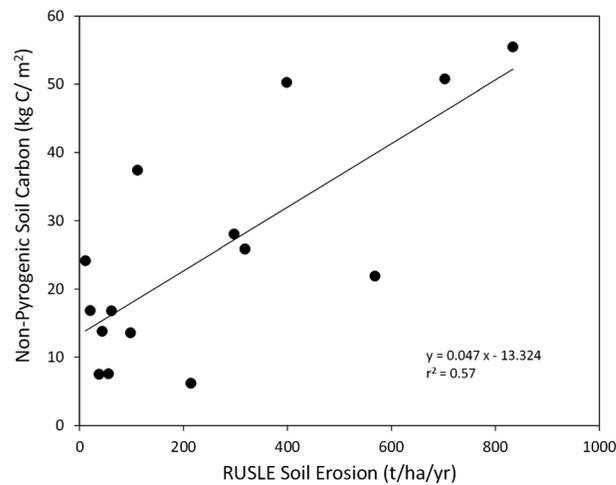


Figure 6. The relationship between soil erosion loss on an annual basis from the RUSLE model in $\text{ton ha}^{-1} \text{yr}^{-1}$ and nonpyrogenic soil organic carbon (kg C m^{-2}) from the BD NMR+ model. The results of a least squares regression based on a linear relationship with regression and coefficient of determination values are presented.

for all biomolecule concentrations (Figure 3). Our finding that the PLSR cross-validation coefficient spectra had peak values near 1581 and 1393 cm^{-1} is consistent for detection of BC based on wave numbers with other studies (Figure 7) [Janik and Skjemstad, 1995]. This is important because MIRS-based spectral models should be associated with mechanistic absorption features associated with aromatic C rather than based on covariance due to the presence of other components such as clay content or other inorganic minerals [Janik et al., 2007].

The results by MIRS predictions of BC, including the biomolecule concentrations, were similar to the predictions by the BD NMR+ model method. However, we found anomalously high average soil BC concentrations values (5 g C kg^{-1} soil) in 2 of 16 of the no fire plots. Detection of BC for sites without recent fire evidence based on fire scarred trees may be considered “legacy BC” in soil from historic fires before the stand initiation (at least 100 years ago). However, the significantly high values we found here are likely due to spectral modeling.

5.2. BC in the Ecosystem

Estimated soil BC values from the BD NMR+ integrated across soil depth produced values that ranged from 0.04 to $1.56 \text{ kg BC m}^{-2}$. With an average value of $0.51 \text{ kg BC m}^{-2}$, soil BC was estimated to comprise $\approx 2\%$ of

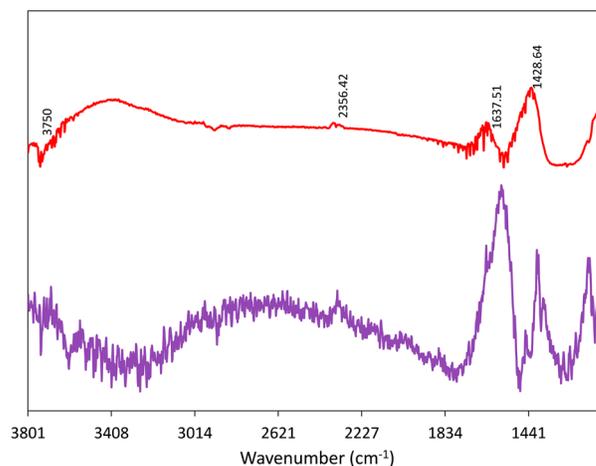


Figure 7. (top) The MIRS spectra of a soil sample with 3.37 g C kg^{-1} soil of black carbon predicted by the BD NMR+ model method is shown (bottom) with the PLSR cross-validation coefficient spectra of the average of first six loading weights for black carbon.

bonds associated with particular chemical functional groups. Data from our MIRS contained fewer mechanistic absorption spectra associated with specific chemical bonds of BC as compared to other studies (Figure 4) [Janik et al., 2007]. This was likely due to higher levels of goethite and calcite in our soil samples, which obscure the MIRS signal of SOM and reduce the predictability of certain organic groups [Janik et al., 1995]. The benefits of PLSR are the significant condensation of information, the ability to incorporate collinear and nonlinearity data sets, and the discrimination between relevant spectral information and systematic error in measurement of spectral noise [Haaland and Thomas, 1988].

The PLSR using the MIRS data coupled with the BD NMR+ model as the reference data for calibration had high prediction accuracy

of the soil C stored in the BCNWR woodland ecosystem [Yao et al., 2012]. Our BC concentration values were similar to those from a temperate mixed-grass savanna of the southern Great Plains of the U.S. that found BC comprised $50\text{--}90 \text{ g C kg}^{-1}$ SOC at $0\text{--}10 \text{ cm}$, and $70\text{--}130 \text{ g C kg}^{-1}$ SOC at $10\text{--}20 \text{ cm}$ [Dai et al., 2005]. In that study, the 2–3 years fire return interval was found to minimally affect BC pool size. By comparison, soils of an Alaskan black spruce forest had BC stocks in surface mineral soil that ranged from 25 g C kg^{-1} SOC to 404 g C kg^{-1} SOC [Kane et al., 2010].

No SOM decomposition differences were found between fire groups (indicated by the NMR data derived Alkyl C/O-Alkyl C ratio), indicating current soil BC decomposition

was limited [Baldock *et al.*, 1997]. Changes in BC during initial addition to mineral soil have been observed as certain microbial groups utilize BC as an energy source referred to as “priming” [Zimmerman *et al.*, 2011]; however, the effect of this loss is generally seen within 1 or 2 years. Our study observed changes in BC over multiple years which are likely due to broader scale processes. Although recent studies have indicated soil BC might have shorter turnover time than has been previously estimated [Alexis *et al.*, 2012; Knicker *et al.*, 2012], vegetation type and climate are important. Wood-derived BC is more resistant to decomposition than grass-derived BC [Singh *et al.*, 2012]. Also, soil BC decomposes slower in drier climate such as found in BCNWR [Nguyen and Lehmann, 2009]. For our study area, soil BC was primarily derived from juniper and oak woody plants that, coupled with the relative dry subhumid, showed little decomposition over the last 100 years on average. No relationship between soil BC concentration, SOM decomposition, or stability (indicated by the lignin/N) were found, indicating that soil BC may have a limited role in soil C turnover in this ecosystem [Melillo *et al.*, 1989]. The differences in BC found in the old fire versus the recent fire sites are related to loss of BC. Black carbon particles, including charcoal, have a mean diameter $< 53 \mu\text{m}$ that may increase physical lability in the soil matrix [Skjemstad *et al.*, 1999]. The BC that remains near the soil surface ($< 10 \text{ cm}$) is likely transported by overland flow during high-precipitation events. Although surface BC may be translocated into lower soil horizons by mass movement of fine-grained soil material (e.g., clay and silt) in addition to biological activity [Dai *et al.*, 2005; Fedoroff *et al.*, 1990], for our study area, soil depth was thin ($< 30 \text{ cm}$), which limits potential deep soil translocation.

Assessment of nonpyrogenic SOC compared to modeled soil erosion showed a positive linear trend (Figure 6) that we explained by considering that sites on plateau tops had thin soils, low soil carbon, and because of the flat terrain, low erosion potential. In contrast, hillsides had deeper, well-developed soils, though with higher erosion potential as a function of topographic slope. This result supports that nonpyrogenic SOC is a “stable” in terms of being constrained normal pedogenic factors such as topography and vegetation. The inverse relationship found for BC and modeled soil erosion highlights the potential erosion potential BC.

The wide range of soil BC concentrations observed in our study may be associated with change in vegetation cover over time, fire histories, and variability of topography in this woodlands. For the BCNWR, fire is prevalent on steep, juniper-dominant southern hillsides due to insolation and differential heating effects of fuels [Murray *et al.*, 2013]. With limited decomposition and soil translocation potential, erosion is likely the dominant mechanism for soil BC loss in our study region because the relatively short duration since fire would not allow for substantial BC mineralization [Czimczik and Masiello, 2007]. With steep average topographic slope of all our study plots ($15.3 \pm 13.9^\circ$), off-site transport of soil BC was likely substantial in this region as indicated by the moderate correlation between modeled plot soil erosion and soil BC concentrations (Figure 4). The RUSLE model captures precipitation impacts on soil erosion in high slope environments represented with the R , β , and λ variables indicating that rainfall may drive soil BC loss in this hilly terrain [Rumpel *et al.*, 2006, 2009].

The inverse relationship found between soil BC and soil erosion highlights the importance of physical stability of soil, which is partially affected by topographic position, is important for soil BC sequestration. In addition, the similar inverse relationship found soil BC and time since fire also indicates the importance of timing of inputs of BC from past fire events.

6. Conclusions and Implications

Soil BC should part of carbon budget estimation due to the potential longevity and concentration of this form of carbon in most terrestrial ecosystems. We found that the BD NMR + model predicted higher concentrations of soil BC for our soil samples with lower mixing model errors and higher estimate accuracies as compared to the CP NMR + model method. The validation of the PLSR calibration showed the ability of MIRS to predict the concentration of biomolecules in soil with accurate calibration data from other prediction methods such as the BD NMR + model method. For prediction of BC using MIRS, we found the signature vibrational frequencies of 1581 and 1393 wave number (cm^{-1}) were consistent with the vibrational frequencies of aromatic C. The MIRS method provides a cost-effective method to estimate average soil BC content, but requires accurate reference data to produce accurate results.

From our analysis, the regional average soil BC concentration was estimated to be around 1.40 g C kg^{-1} soil ($0.51 \text{ kg BC m}^{-2}$) and represents over 2% of soil organic C in this ecosystem. There were significant differences of the soil BC concentrations between the fire-affected sites and no-fire-affected sites. Little evidence of significant

decomposition loss of soil BC was found indicating that soil BC is lost from these woodlands primarily due to soil erosion. This results support observations that effective soil BC residence time is on the order of hundreds of years, rather than thousands of years, due to significant off-site transportation [Alexis *et al.*, 2012; Knicker *et al.*, 2012; Singh *et al.*, 2012]. Future assessment of soil BC should consider the potential of BC transportation due to erosion and the frequency of fires as key for constraining expectation of long-term site retention.

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References

- 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*, 189–190, 98–107, doi:10.1016/j.geoderma.2012.05.003.
- Alexis, M., D. Rasse, C. Rumpel, G. Bardoux, N. Péchot, P. Schmalzer, B. Drake, and A. Mariotti (2007), Fire impact on C and N losses and charcoal production in a scrub oak ecosystem, *Biogeochemistry*, 82(2), 201–216, doi:10.1007/s10533-006-9063-1.
- 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 ¹³C NMR spectroscopy, *Aust. J. Soil Res.*, 35, 1061–1083.
- Baldock, J. A., C. A. Masiello, Y. Gélinas, and J. I. Hedges (2004), Cycling and composition of organic matter in terrestrial and marine ecosystems, *Mar. Chem.*, 92(1–4), 39–64, doi:10.1016/j.marchem.2004.06.016.
- Bornemann, L., G. Welp, S. Brodowski, A. Rodionov, and W. Amelung (2008), Rapid assessment of black carbon in soil organic matter using mid-infrared spectroscopy, *Org. Geochem.*, 39(11), 1537–1544, doi:10.1016/j.orggeochem.2008.07.012.
- Cadet, F., and B. Offmann (1996), Baseline correction applied to a biological: Mid-infrared spectra collection, *Spectrosc. Lett.*, 29(4), 591–607.
- Chapin, F. S., P. A. Matson, and H. A. Mooney (2002), *Principles of Terrestrial Ecosystem Ecology*, Springer, New York.
- Colthup, N. B., L. H. Daly, and S. E. Wilberley (1990), *Introduction to Infrared and Raman Spectroscopy*, Academic, New York.
- Czimczik, C. I., and C. A. Masiello (2007), Controls on black carbon storage in soils, *Global Biogeochem. Cycles*, 21, GB3005, doi:10.1029/2006GB002798.
- Dai, X., T. W. Boutton, B. Glaser, R. J. Ansley, and W. Zech (2005), Black carbon in a temperate mixed-grass savanna, *Soil Biol. Biochem.*, 37(10), 1879–1881, doi:10.1016/j.soilbio.2005.02.021.
- Diamond, D. D. (1997), *An Old-Growth Definition for Western Juniper Woodlands: Texas Ashe Juniper Dominated or Codominated Communities*, Gen. Tech. Rep. SRS-15, 15 pp., U.S. Department of Agriculture, Forest Service, Southern Research Station, Asheville, N. C.
- Efron, B. (2004), The estimation of prediction error, *J. Am. Stat. Assoc.*, 99(467), 619–632, doi:10.1198/016214504000000692.
- Fedoroff, S. D., F. E. Smeins, and M. L. Thompson (1990), Micromorphological evidence of paleoenvironmental change in Pleistocene and Holocene paleosols, in *Developments in Soil Science*, vol. 19, edited by L. A. Douglas, pp. 653–665, Elsevier, Berlin, doi:10.1016/S0166-2481(08)70382-9.
- Forbes, M. S., R. J. Raison, and J. O. Skjemstad (2006), Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems, *Sci. Total Environ.*, 370(1), 190–206, doi:10.1016/j.scitotenv.2006.06.007.
- Fuhlendorf, S. D., F. E. Smeins, and W. E. Grant (1996), Simulation of a fire-sensitive ecological threshold: A case study of Ashe juniper on the Edwards Plateau of Texas, USA, *Ecol. Model.*, 90(3), 245–255, doi:10.1016/0304-3800(95)00151-4.
- Gehlbach, F. R. (1988), Forests and woodlands of the northeastern Balcones escarpment, in *Edwards Plateau Vegetation: Plant Ecological Studies in Central Texas*, edited by B. B. Amos and F. R. Gehlbach, pp. 57–77, Baylor Univ. Press, Waco, Tex.
- Geladi, P., and B. R. Kowalski (1986), Partial least-squares regression: A tutorial, *Anal. Chim. Acta*, 185, 1–17, doi:10.1016/0003-2670(86)80028-9.
- Gonçalves, C. N., R. S. D. Dalmolin, D. P. Dick, H. Knicker, E. Klamt, and I. Kögel-Knabner (2003), The effect of 10% HF treatment on the resolution of CPMA ¹³C NMR spectra and on the quality of organic matter in ferralsols, *Geoderma*, 116(3–4), 373–392, doi:10.1016/S0016-7061(03)00119-8.
- Haaland, D. M., and E. V. Thomas (1988), Partial least-squares methods for spectral analyses. 1. Relation to other quantitative calibration methods and the extraction of qualitative information, *Anal. Chem.*, 60(11), 1193–202.
- Hammes, K., R. J. Smernik, J. O. Skjemstad, A. Herzog, U. F. Vogt, and M. W. I. Schmidt (2006), Synthesis and characterisation of laboratory-charred grass straw (*Oryza sativa*) and chestnut wood (*Castanea sativa*) as reference materials for black carbon quantification, *Org. Geochem.*, 37(11), 1629–1633, doi:10.1016/S0016-7061(03)00119-8.
- Hammes, K., *et al.* (2007), Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere, *Global Biogeochem. Cycles*, 21, GB3016, doi:10.1029/2006GB002914.
- 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, doi:10.2136/sssaj2001.1853.
- Hockaday, W. C., A. M. Grannas, S. Kim, and P. G. Hatcher (2007), The transformation and mobility of charcoal in a fire-impacted watershed, *Geochim. Cosmochim. Acta*, 71(14), 3432–3445, doi:10.1016/j.gca.2007.02.023.
- Janik, L. J., and J. O. Skjemstad (1995), Characterization and analysis of soils using mid-infrared partial least-squares. 2. Correlations with some laboratory data, *Soil Res.*, 33(4), 637–650, doi:10.1071/SR9950637.
- Janik, L. J., J. O. Skjemstad, and M. D. Raven (1995), Characterization and analysis of soils using mid-infrared partial least-squares. 1. Correlations with XRF-determined major-element composition, *Soil Res.*, 33(4), 621–636, doi:10.1071/SR9950621.
- Janik, L. J., R. H. Merry, and J. O. Skjemstad (1998), Can mid infrared diffuse reflectance analysis replace soil extractions?, *Aust. J. Exp. Agric.*, 38(7), 681–696, doi:10.1071/EA97144.
- Janik, L. J., J. O. Skjemstad, K. D. Shepherd, and L. R. Spouncer (2007), The prediction of soil carbon fractions using mid-infrared-partial least square analysis, *Aust. J. Soil Res.*, 45(2), 73–81, doi:10.1071/SR06083.
- Kane, E., W. Hockaday, M. Turetsky, C. Masiello, D. Valentine, B. Finney, and J. Baldock (2010), Topographic controls on black carbon accumulation in Alaskan black spruce forest soils: Implications for organic matter dynamics, *Biogeochemistry*, 100(1), 39–56, doi:10.1007/s10533-009-9403-z.
- Knicker, H., and H. Lüdemann (1995), N-15 and C-13 CPMA and solution NMR studies of N-15 enriched plant material during 600 days of microbial degradation, *Org. Geochem.*, 23(4), 329–341, doi:10.1016/0146-6380(95)00007-2.
- Knicker, H., R. Nikolova, D. P. Dick, and R. S. D. Dalmolin (2012), Alteration of quality and stability of organic matter in grassland soils of southern Brazil highlands after ceasing biannual burning, *Geoderma*, 181–182(0), 11–21, doi:10.1016/j.geoderma.2012.03.001.
- Kouli, M., P. Soudos, and F. Vallianatos (2009), Soil erosion prediction using the Revised Universal Soil Loss Equation (RUSLE) in a GIS framework, Chania, Northwestern Crete, Greece, *Environ. Geol.*, 57, 483–497, doi:10.1007/s00254-008-1318-9.
- Kuhlbusch, T. A. J., and P. J. Crutzen (1995), Toward a global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO₂ and a source of O₂, *Global Biogeochem. Cycles*, 9(4), 491–501, doi:10.1029/95GB02742.
- Lehmann, J., J. Gaunt, and M. Rondon (2006), Bio-char sequestration in terrestrial ecosystems – A review, *Mitig. Adapt Strat. Gl.*, 11(2), 395–419, doi:10.1007/s11027-005-9006-5.

- Liang, B., J. Lehmann, D. Solomon, S. Sohi, J. E. Thies, J. O. Skjemstad, F. J. Luizão, M. H. Engelhard, E. G. Neves, and S. Wirick (2008), Stability of biomass-derived black carbon in soils, *Geochim. Cosmochim. Acta*, *72*(24), 6069–6078, doi:10.1016/j.gca.2008.09.028.
- 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, doi:10.2136/sssaj2007.0363.
- Masiello, C. A. (2004), New directions in black carbon organic geochemistry, *Mar. Chem.*, *92*(1–4), 201–213, doi:10.1016/j.marchem.2004.06.043.
- McCune, B., and J. B. Grace (2002), *Analysis of Ecological Communities*, MjM Software, Gleneden Beach, Oreg.
- 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*, *118*, 189–198, doi:10.1007/978-94-009-1021-8_6.
- Murray, D., J. D. White, and J. Yao (2013), Loss of neighbors, fire, and climate effects on Texas red oak growth in a juniper-dominated woodland ecosystem, *Am. Midl. Nat.*, *170*(2), 348–369, doi:10.1674/0003-0031-170.2.348.
- National Climatic Data Center (2011), Climate data online, National Climate Data Center, National Oceanic and Atmospheric Administration, Asheville, N. C.
- Nelson, P. N., and J. A. Baldock (2005), Estimating the molecular composition of a diverse range of natural organic materials from solid-state ^{13}C NMR and elemental analyses, *Biogeochemistry*, *72*(1), 1–34, doi:10.1007/s10533-004-0076-3.
- Nelson, P. N., A. Baldock, J. M. Oades, G. J. Churchman, and P. Clarke (1999), Dispersed clay and organic matter in soil: Their nature and associations, *Soil Res.*, *37*(2), 289–316, doi:10.1071/S98076.
- Nguyen, B. T., and J. Lehmann (2009), Black carbon decomposition under varying water regimes, *Org. Geochem.*, *40*(8), 846–853, doi:10.1016/j.orggeochem.2009.05.004.
- Preston, C. M., and M. W. I. Schmidt (2006), Black (pyrogenic) carbon: A synthesis of current knowledge and uncertainties with special consideration of boreal regions, *Biogeosciences*, *3*(4), 397–420.
- Preston, C. M., M. Schnitzer, and J. A. Ripmester (1989), A spectroscopic and chemical investigation on the de-ashing of a humin, *Soil Sci. Soc. Am. J.*, *53*(5), 1442–1447, doi:10.2136/sssaj1989.03615995005300050023x.
- Reeves, J. B., G. W. McCarty, D. W. Rutherford, and R. L. Wershaw (2008), Mid-infrared diffuse reflectance spectroscopic examination of charred pine wood, bark, cellulose, and lignin: Implications for the quantitative determination of charcoal in soils, *Appl. Spectrosc.*, *62*(2), 182–189.
- Renard, K. G., and J. R. Freimund (1994), Using monthly precipitation data to estimate the R factor in the revised USLE, *J. Hydrol.*, *157*, 287–306, doi:10.1016/0022-1694(94)90110-4.
- Renard, K. G., G. A. Foster, G. A. Wessies, D. K. McCool, and D. C. Yoder (1997), *Predicting Soil Erosion by Water: A Guide to Conservation Planning With the Revised Universal Soil Loss Equation (RUSLE)*, USDA Agriculture Handbook, vol. 703, 404 pp., Government Printing Office, Washington, D. C.
- Rodionov, A., W. Amelung, N. Peinemann, L. Haumaier, X. Zhang, M. Kleber, B. Glaser, I. Urusevskaya, and W. Zech (2010), Black carbon in grassland ecosystems of the world, *Global Biogeochem. Cycles*, *24*, GB3013, doi:10.1029/2009GB003669.
- Rumpel, C., M. Alexis, A. Chabbi, V. Chaplot, D. P. Rasse, C. Valentin, and A. Mariotti (2006), Black carbon contribution to soil organic matter composition in tropical sloping land under slash and burn agriculture, *Geoderma*, *130*(1–2), 35–46, doi:10.1016/j.geoderma.2005.01.007.
- Rumpel, C., A. Ba, F. Darboux, V. Chaplot, and O. Planchon (2009), Erosion budget and process selectivity of black carbon at meter scale, *Geoderma*, *154*(1–2), 131–137, doi:10.1016/j.geoderma.2009.10.006.
- Schmidt, M. W. I., H. Knicker, P. G. Hatcher, and I. Kogel-Knabner (1997), Improvement of ^{13}C and ^{15}N CPMAS NMR spectra of bulk soils, particle size fractions and organic material by treatment with 10% hydrofluoric acid, *Eur. J. Soil Sci.*, *48*(2), 319–328, doi:10.1111/j.1365-2389.1997.tb00552.x.
- Simpson, M. J., and P. G. Hatcher (2004), Determination of black carbon in natural organic matter by chemical oxidation and solid-state ^{13}C nuclear magnetic resonance spectroscopy, *Org. Geochem.*, *35*(8), 923–935, doi:10.1016/j.orggeochem.2004.04.004.
- Singh, N., S. Abiven, M. S. Torn, and M. W. I. Schmidt (2012), Fire-derived organic carbon in soil turns over on a centennial scale, *Biogeosciences*, *9*(8), 2847–2857, doi:10.5194/bg-9-2847-2012.
- Skjemstad, J. O., J. A. Taylor, and R. J. Smernik (1999), Estimation of charcoal (char) in soils, *Commun. Soil Sci. Plant Anal.*, *30*(15–16), 2283–98, doi:10.1080/00103629909370372.
- Smernik, R. J., and J. M. Oades (2000), The use of spin counting for determining quantitation in solid state ^{13}C NMR spectra of natural organic matter: 1. Model systems and the effects of paramagnetic impurities, *Geoderma*, *96*(1–2), 101–129, doi:10.1016/S0016-7061(00)00006-9.
- Smernik, R. J., and J. M. Oades (2003), Spin accounting and RESTORE? Two new methods to improve quantitation in solid-state ^{13}C NMR analysis of soil organic matter, *Eur. J. Soil Sci.*, *54*(1), 103–116, doi:10.1046/j.1365-2389.2003.00497.x.
- Stroup, W. W., and J. Stubbendieck (1983), Multivariate statistical methods to determine changes in botanical composition, *J. Range Manage.*, *36*(2), 208–212.
- United States Department of Agriculture, Natural Resources Conservation Service (1974), *Soil Survey of Travis County*, USDA, Natural Resources Conservation Service, Tex.
- Viscarra Rossel, R. A., D. J. J. Walvoort, A. B. McBratney, L. J. Janik, and J. O. Skjemstad (2006), Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties, *Geoderma*, *131*(1–2), 59–75, doi:10.1016/j.geoderma.2005.03.007.
- Wischmeier, W. H., and D. D. Smith (1978), *Predicting Rainfall Erosion Losses—A Guide to Conservation Planning*, Agricultural Handbook, vol. 537, 67 pp., U.S. Department of Agriculture, Washington.
- Yao, J., D. B. Murray, A. Adhikari, and J. D. White (2012), Fire in a sub-humid woodland: The balance of carbon sequestration and habitat conservation, *For. Ecol. Manage.*, *280*, 40–51, doi:10.1016/j.foreco.2012.05.042.
- Zimmerman, A. R., B. Gao, and M.-Y. Ahn (2011), Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils, *Soil Biol. Biochem.*, *43*, 1169–1179, doi:10.1016/j.soilbio.2011.02.005.