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# Black carbon in a temperate mixed-grass savanna

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**Abstract**

Black carbon (BC) or charcoal is thought to represent an important component of the carbon cycle, but has seldom been quantified in soils. We quantified soil BC in a temperate mixed-grass savanna in the southern Great Plains using benzenecarboxylic acids as molecular markers for BC. Soils were collected from four fire treatments (repeated summer fires in 1992 and 1994; repeated winter fires in 1991, 1993 and 1995; alternate-season fires in winter 1991, summer 1992, and winter 1994; and unburned control) at 0–10 and 10–20 cm depth in 1996. Black carbon concentrations ranged from 50 to 130 g BC $kg^{-1}$ of soil organic carbon (SOC), or from 0.55 to 1.07 g BC $kg^{-1}$ of whole soil in this mixed grass savanna. The BC contribution to SOC increased significantly with soil depth ($P<0.05$). Repeated fires increased BC slightly compared to the unburned controls; however, the effects of repeated fires on BC were not statistically significant in this mixed-grass savanna. Results of this study provide estimates of BC concentrations for native, uncultivated mixed-grass savanna, and indicate that 2–3 fires have little effect on the size of the soil BC pool in this region.


*Keywords:* Black carbon; Prescribed fire; Mixed-grass savanna; Soil carbon sequestration; Soil organic carbon; Benzenecarboxylic acids; Charcoal; Carbon cycle

Fires affect more than 400 Mha of grassland, savanna, and forest each year, and transfer approximately 1.7–4.1 Pg ($10^{15}$ g) of carbon (Lavorel et al., 2001) to the atmosphere annually. In addition, incomplete combustion of biomass results in the storage of approximately 0.05–0.2 Pg C $yr^{-1}$ as highly refractory black carbon (BC) or charcoal in soils (Kuhlbusch, 1998; Schmidt and Noack, 2000). Because BC has a highly aromatic structure with few functional groups, it is resistant to decay and therefore contributes to the recalcitrant fraction of soil carbon. At the global scale, formation of BC transfers fast-cycling C from the atmosphere-biosphere system to much slower-cycling geological forms that may persist for millenia, and therefore represents a sink for atmospheric $CO_2$ (Kuhlbusch, 1998; Masiello and Druffel, 1998). It has been hypothesized that BC may comprise a significant fraction of the 'missing carbon' in global C budget (Kuhlbusch, 1998). Despite this potential significance, BC has seldom been quantified in soils, especially in those with a known fire history.

Prescribed fires are often utilized to manage and manipulate vegetation composition in many ecosystems around the world. In North American rangelands, fires are commonly employed to prevent or slow woody plant encroachment into grasslands and savannas (Wright and Bailey, 1982; Scholes and Archer, 1997; Ansley and Jacoby, 1998). However, the quantity and quality of charred organic compounds generated by these fires, and their influence on soil organic carbon (SOC) pools and fluxes in rangeland soils have received little attention. Few studies have quantified BC in North American soils, and existing estimates have emphasized the northern half of the continent (Ponomarenko and Anderson, 2001; Glaser and Amelung, 2003) and/or cultivated soils (Skjemstad et al., 2002). No studies have been conducted at sites with known recent fire histories. Therefore, the purpose of this study was to quantify BC in an uncultivated, native temperate mixed-grass savanna located in the southern Great Plains and subjected to fires applied at different times of the year.

Soil samples were collected at 0–10 and 10–20 cm depths at the Texas Agricultural Experiment Station Waggoner

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Ranch (33°51′20″N, 99°26′50″W) near Vernon in northern Texas in December 1996. Prior to burning, vegetation was a mixture of $C_3$ and $C_4$ grass species in the herbaceous layer, and *Prosopis glandulosa* (honey mesquite) in the tree layer. Livestock grazing was excluded from the study area since 1988, and fire was excluded for at least 30 yr prior to the establishment of fire treatments in 1991. This study utilized four fire treatments, each consisting of three replicates: (1) repeated summer fires in 1992, 1994 (SF); (2) repeated winter fires in 1991, 1993, 1995 (WF); (3) alternate-season fires in winter 1991, summer 1992, and winter 1994 (SWF); and (4) an unburned control. Plot size for each replicate ranged from 1 to 6 ha. All treatments were on the same soil type (fine, mixed, thermic Typic Paleustolls of the Tillman series) on level, upland surfaces. Soil samples were taken within small patches of *Nasella leucotricha* (a perennial $C_3$ bunchgrass) in grassland interstitial spaces between mesquite trees. Ten 2.5 cm dia soil cores were collected in each plot and mixed into two subsamples (five cores per subsample) prior to analysis. Litter was removed from the soil surface before coring. Samples were oven-dried at 50 °C for 24 h and sieved (2 mm) to remove coarse roots and plant debris; however, all mineral portions of the soil as well as fine roots passed through the sieve. Soils were then homogenized thoroughly and pulverized (<50 μm) for analysis of C concentrations and BC.

Soil organic C concentrations were determined by dry combustion/gas chromatography using a Carlo Erba EA-1108 (CE Elantech, Lakewood, NJ) elemental analyzer. Samples containing $CaCO_3$ were pretreated with HCl (Nieuwenhuize et al., 1994), and organic C concentrations were expressed on a whole-soil basis. Black carbon was analyzed using benzenepolycarboxylic acids (BPCA) as molecular markers (Glaser et al., 1998; Glaser and Amelung, 2003). The procedure includes metal removal (4M TFA, 105 °C, 4 h), acid oxidation ($HNO_3$ 65%, 170 °C, 8 h), sample cleanup (residual metal removal with Dowex 50W-X8, 200–400 mesh), derivatization, and gas chromatography with flame ionization detection. The major advantage of this method is that nitric acid completely breaks down the highly aromatic core of BC and leads to the formation of BPCA; except for charred materials, no other thermally unaltered materials can form BPCA after the oxidation.

Data were analyzed using a general linear model in a split plot design with fire treatment as the whole plot, soil depth as the split plot, and core as a random factor (SPSS, 2004). Mean comparisons were performed using Fisher's LSD with Bonferroni adjustment.

Soil organic C ranged from $7.2 \pm 0.6$ to $12.4 \pm 1.4$ g C $kg^{-1}$, and decreased significantly with soil depth ($P < 0.001$) (Fig. 1a). SF and SWF enhanced SOC significantly ($P < 0.001$) compared to the unburned controls and WF at 0–10 cm depth, but not at 10–20 cm depth. This increase in SOC storage is likely due to increased primary production in the fire treatments. Ansley et al. (2002) showed that photosynthetic rates of *Prosopis glandulosa*

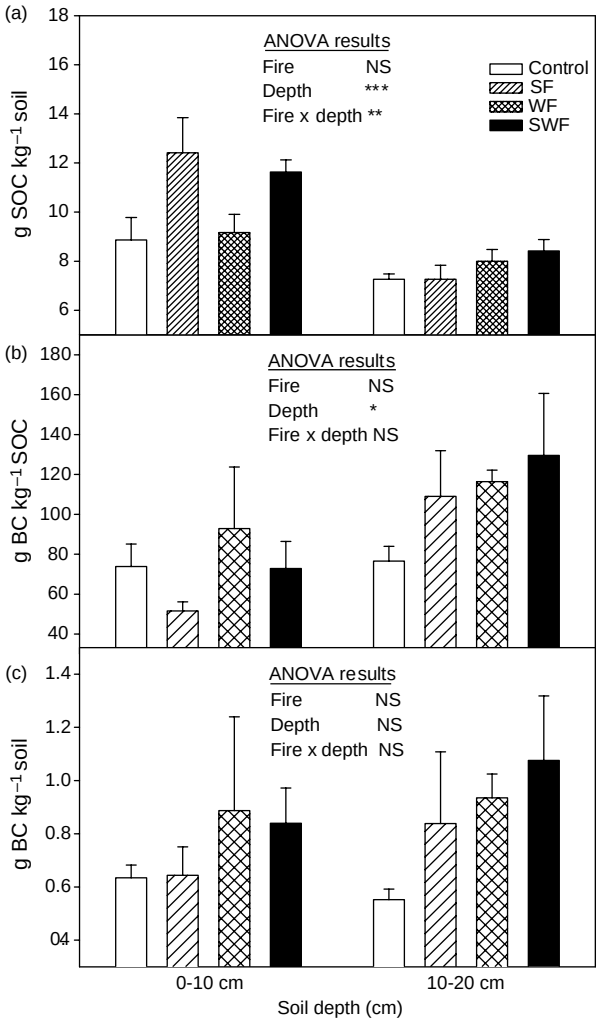


Fig. 1. Soil organic C (SOC) concentration (g SOC $kg^{-1}$ soil) (a), black carbon (BC) as a proportion of SOC (g BC $kg^{-1}$ SOC) (b), and BC as a proportion of whole soil (g BC $kg^{-1}$ soil) (c) at 0–10 (left side) and 10–20 (right side) cm depths. Error bars are standard error. $^{*}P < 0.05$, $^{**}P < 0.01$, $^{***}P < 0.001$. NS, not significant.

regrowing after fire can be 3× those of unburned plants; some of that increased photosynthetic production may be allocated to increased root production by the woody component of this savanna. In addition, recent studies adjacent to this study area have shown that root production by grasses is significantly greater in fire treatments than in unburned controls (J.A. Hubbard, unpub. PhD thesis, Texas A&M University, 2003). Therefore, it seems probable that observed differences in SOC may be attributable to increased root productivity by both woody and herbaceous components of this savanna in response to fire.

Black carbon as a proportion of SOC ranged from $51 \pm 4.6$ to $129 \pm 31$ g BC $kg^{-1}$ SOC (Fig. 1b), and increased significantly with soil depth ($P < 0.05$). Fire treatment had no consistent effects on the BC concentration of SOC at the 0–10 cm depth, but increased the BC concentration of SOC at the depth of 10–20 cm compared to that of the unburned control. Black carbon as a proportion of whole soil weight

ranged from $0.55 \pm 0.4$ to $1.07 \pm 0.2$ g $kg^{-1}$ and increased slightly with soil depth in fire treatment but not the control (Fig. 1c). Fire increased BC concentration of soil at both depths; however, neither fire treatments nor soil depth had a significant effect on BC concentration of whole soil.

Black carbon comprised 5–9% of the SOC at 0–10 cm, and 7–13% at 10–20 cm in this mixed-grass savanna. The contribution of BC to SOC from 0 to 10 cm is comparable to the results reported by Glaser and Amelung (2003). They measured BC in 18 native grassland top soil samples (0–10 cm) from central Saskatchewan to southern Texas using the same analytical method. Four out of their five samples from southern Texas had percentage of BC to SOC ranging from 8 to 11%. Skjemstad et al. (2002) measured charcoal in five US agricultural soils using a combination of physical fractionation, high energy photo-oxidation and solid-state $^{13}C$ NMR spectroscopy. Charcoal represented 1.8–13.6 g $kg^{-1}$ of soil, and 10–35% of SOC, similar to their results from Australian soils (Skjemstad et al., 1999a). However, it is very difficult to compare results between methods because different methods measure different fractions of the BC continuum (Schmidt et al., 2001). Based on differences between controls and fire treatments at 0–10 cm, we estimate that BC is produced at rates of approximately 5, 87, and 70 mg C $kg^{-1}$ soil per fire in SF, WF, and SWF treatments, respectively. Black carbon accumulation rates at 10–20 cm were 145, 130, and 180 mg C $kg^{-1}$ soil per fire in SF, WF, and SWF treatments, respectively, although the differences between the controls and the fire treatments were not significant. The higher rates of accumulation of BC at 10–20 cm suggest that BC is translocated into lower horizons. Potential mechanisms of movement might include mass movement with clay and silt, and biological activity (Federoff et al., 1990). Skjemstad et al. (1999a) have shown that essentially all BC is $<53$ μm. Hence, this finely divided material should be relatively mobile and capable of moving into the same portion of the profile where clay and silt accumulate (Skjemstad et al., 1999b).

Our results indicate that although 2–3 fires significantly increased SOC in the fire treatments, there were only minor effects on the size of the soil BC pool in this region. These data also provide estimates of BC concentrations for native, uncultivated mixed-grass savanna representative of the southern Great Plains region. Since BC likely represents a significant proportion of the recalcitrant SOC pool, these measurements will also contribute to the parameterization of ecosystem biogeochemistry models that are strongly dependent on the size of the recalcitrant pool (Falloon and Smith, 2000; Falloon et al., 2000).

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