Charcoal Carbon in U.S. Agricultural Soils

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ABSTRACT

High levels of charcoal C resulting from repeated historical burning of grasslands, open woodlands, and agricultural crop residues have been reported in soils from Australia and Germany. In this study, five U.S. soils were selected from long-term research plots in widely different agricultural areas. The charcoal C content was estimated on each soil using a combination of physical separation, high energy photo-oxidation and solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. These analyses showed that all five soils contained measurable amounts of charcoal C, <53 μm in size and ranging from 1.8 to 13.6 g C kg^{-1} soil and constituted up to 35% of the soil total organic C (TOC). Scanning electron microscopy showed that the charcoal material had a plant-like morphology but were blocky and had fractured edges. These particles were similar in morphology to those separated from Australian and German soils. The implications of this material, which must be highly resistant to microbiological decomposition, to the soil C cycle are discussed.

Global climate change in relation to the global C cycle is a focus of concern because temperature increases and drought could occur over present agricultural production areas. Agricultural soils play a key role in C cycling and can act as a source or sink of C and thereby impact greenhouse gas emissions. Carbon loss can also affect soil productivity, soil quality, nutrient cycling, soil fertility, and ultimately crop production. In agricultural production systems, C loss may occur as a result of biomass burning, intensive tillage or cultivation, or crop residue removal. Charcoal generated by fires can constitute up to 8 g C kg^{-1} soil and represent up to 30% of the soil organic C content of Australian soils (Skjemstad et al., 1996). Charcoal is an impure form of C produced by incomplete biomass burning or fossil fuel combustion (Goldberg, 1985).

Microorganisms cannot use charcoal as an effective energy source and as a result, charcoal does not contribute to soil biological activity or soil organic matter formation (Albrecht et al., 1995; Seiler and Crutzen, 1980). As TOC declines due to cultivation, the more resistant charcoal fraction increases as a portion of the total C (Skjemstad et al., 2001). Thus, considerable amounts of charcoal could accumulate over the course of centuries or millennia (Zech and Guggenberger, 1996). Despite the apparent importance of charcoal in the environment, there are many uncertainties about its amount and function in soil (Goldhammer, 1990; Dickson and Krankina, 1993; Price et al., 1998).

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Despite few workers recording black C or charcoal in soils from the USA, historically fire has been extensive in the North American grasslands. For example, Collins (1990) reported that because of "periodic droughts, high temperatures, and strong winds, the North American grasslands provide an ideal environment for ignition and perpetuation of fire." Collins (1990) also concluded that "most evidence suggests that Indians frequently started grassland fires to modify habitat and either drive or attract wild game" and that "fires, caused by human activity or otherwise, were historically a frequent component of the disturbance regime in grasslands." It might be expected therefore that a legacy of this frequent burning would be the presence of significant quantities of charcoal in the soil profiles under this activity.

The objective of this work was to determine the range of charcoal content from a number of U.S. agricultural soils. Five soils, collected from long-term research sites, were selected for charcoal analyses because of their contrasting properties and organic matter contents. We report the nature and amount of charcoal in these soils and discuss the relative significance in agriculture systems.

MATERIALS AND METHODS

The five soils selected for this study were from long-term research plots in widely different agricultural areas. Selected properties of the soils are summarized in Table 1. Brennyville silt loam (coarse-loamy, mixed, superactive, frigid Aquic Glossudalfs) was sampled from a farm near Milaca, MN (45°45′28″ N, 93°3′55″ W). The surface horizon is generally dark gray or pale brown with low organic matter content and formed in a silty mantle of loess or lacustrine deposits. Brennyville soils are moderately well drained with moderate permeability in the silty mantle. Corn (*Zea mays* L.) is typically grown at the collection site and soils are occasionally limed.

Elliott silt loam (fine, illitic, mesic Aquic Argiudoll) was a standard soil chosen by the International Humic Substances Society (IHSS) and collected near Joliet, Illinois (41°31′36″ N, 88°7′20″ W). Elliott soils are very deep and poorly drained soils on moraines and till plains. Permeability is generally slow. The Ap horizon is a black silt loam and moderately acid. Corn and soybean (*Glycine Max.* L.) are typically grown and soils are occasionally limed. More information about humic substance extraction from Elliott soil for the IHSS collection can be found at www.ihss.gatech.edu/history.html (verified 11 Mar. 2002).

Houston Black clay (fine, smectitic, thermic Udic Haplusterts) was collected from USDA-ARS experimental plots in Temple, TX (31°5′5″ N, 97°21′48″ W). The series consists of very deep, moderately well-drained, very slowly permeable soils that formed from weakly consolidated calcareous clays and marls of Cretaceous Age. The A1 horizon is a very dark gray clay. The soil sample used was collected from a site that

Abbreviations: CP, cross polarization; EDX, energy dispersive x-ray; IHSS, Internation Humic Substance Society; MAS, magic angle spin; NMR, nuclear magnetic resonace; OC, organic C; SEM, scanning electron microscopy; TOC, total OC.

Table 1. Soil descriptions and properties (0–20 cm depth).

Soil series name	pH†	Total C‡	IC‡	N†	Clay§	Clay	CEC§
	H_2O	g kg^{-1}			%	mineral type§	m_c 100 g^{-1}
Brennyville silt loam	6.2	18.6	ND¶	1.8	5–16	Mixed	3–18
Elliott silt loam	6.5	28.7	ND	2.7	35–45	Illitic	20–24
Houston Black clay	7.6	87.5	50.6	2.2	40–60	Montmorillonitic	39–62
Vallers silty clay loam	7.6	41.3	ND	3.4	28–35	Mixed	15–28
Walla Walla silt loam	5.8	10.3	ND	0.8	10–17	Mixed	12–20

† USDA-ARS test results.
‡ CSIRO Land & Water test results, IC, inorganic C.
§ From soil interpretive summaries.
¶ ND = not detected.

was undisturbed prairie for the last 30 yr. Cotton (*Gossypium hirisutum* L.), corn, sorghum [*Sorghum bicolor* (L.) Moench], and wheat (*Triticum aestivum* L.) are typical crops grown on Houston Black clay. Research findings are described by Reicosky et al. (1997).

Vallers silty clay loam (fine-loamy, mixed, superactive, frigid Typic Calciaquoll) was collected from the USDA-ARS Swan Lake Research Farm near Morris, MN (45°43′9″ N, 95°4′55″ W). The surface horizon is generally very dark with high organic matter formed in calcareous loamy glacial till. Vallers soils have moderately slow permeability and are found in lower areas of the soil landscape. Corn, soybean, and wheat are typical crops grown. Carbon dioxide flux measurements from Vallers soil have been evaluated by Reicosky (1995).

Walla Walla silt loam (coarse-silty, mixed, superactive, mesic Typic Haploxeroll) soil was obtained from USDA-ARS Columbia Plateau Conservation Research Center from the Crop Residue Plots near Pendleton, OR (45°43′12″ N, 118°0′3″ W). Walla Walla soils, formed on hills, are deep, well-drained, and have moderate permeability. The surface horizon is generally dark grayish brown. The crop rotation was winter wheat-fallow, the tillage was conventional (moldboard plow) and treatment was 90 kg N ha^{-1} with no residue burning (Albrecht et al., 1995; Rasmussen and Smiley, 1997).

Laboratory Procedures

Separation of Physical Fractions

Soil samples were separated into <53- and >53-μm fractions similar to the method described by Cambardella and Elliot (1992). The samples (10 g) were shaken overnight with 50 mL of sodium hexametaphosphate (5 g L^{-1}) before being passed through a 200-μm and a 53-μm sieve in series. The samples were worked in the sieves with a spatula to ensure that no aggregates were retained. The >53-μm fractions were dried, weighed, and inspected under a microscope to ensure that no aggregates or larger pieces of charcoal were retained. The <53-μm suspension was made to 500 mL with water and retained for further analysis.

Photo-oxidations

High energy ultraviolet photo-oxidation was used to remove the more labile fractions of organic matter in the <53-μm fractions. Aliquots (<20 mL) containing between 2 and 3 mg C were placed in quartz tubes, made to 20 mL with water and placed in the photo-oxidizer. The apparatus used for photo-oxidation consisted of a vent, hood, 2.5 kW Hg vapor lamp, stainless steel capillary for air, stainless steel cold finger condensers for sample cooling in an aluminum reactor housing fitted with a light trap (Skjemstad et al., 1994b). Air was passed into the suspensions through the stainless steel tubes at a rate of 50 mL min^{-1} and the samples exposed for 2 h after full power had been reached.

Scanning Electron Microscopy

After treatment, scanning electron microscopy (SEM) was carried out on a Cambridge Stereoscan[1] S250 (Altran Corp., Boston, MA) on samples coated with 20 nm of C. Elemental characterization was performed using a Link AN1000 energy dispersive X-ray (EDX) analyzer. The SEM was used to identify the wood-like morphology of the charcoal particles while the EDX analyzer was used to establish that these pieces were organic and not of mineral origin.

Demineralization of Fractions

The presence of magnetic and paramagnetic materials such as Fe, a common element in soils, can cause severe interference with the NMR technique. All samples used for charcoal estimates were therefore treated with 2% (wt./vol.) HF solution prior to NMR analysis (Skjemstad et al., 1994a). This technique effectively removes Fe and other interfering elements and also concentrates the organic fraction through the selective removal of minerals thereby increasing sensitivity of the technique.

Solid-State Carbon-13 Cross Polarization and Magic Angle Spin Nuclear Magnetic Resonance Analysis

Treated samples were packed into 7-mm zirconia rotors and solid-state ^{13}C Cross Polarization/Magic Angle Spin (CP/MAS) NMR spectra obtained at 50.3 MHz on a Varian Unity 200 spectrometer with a 2.7 T wide-bore Oxford superconducting magnet using a Doty Scientific MAS probe. Instrument conditions were identical to those reported by Skjemstad et al. (1994a). The chemical shift regions 0 to 45, 45 to 110, 110 to 140, 140 to 165, 165 to 190, and 190 to 220 ppm were assigned to alkyl-C, O-alkyl-C, aryl-C, O-aryl-C, carbonyl-C, and aldehyde/ketone-C, respectively (Wilson, 1987; Skjemstad et al., 1996).

Charcoal Estimates

Charcoal content of the <53-μm fractions was estimated using the aryl content of the samples following photo-oxidation as described by Skjemstad et al. (1999). Briefly, the method estimates charcoal as the aryl fraction of the sample, corrected for lignin and lignin-like structures if required and also corrected for the inefficiency of the CP/MAS technique for highly unsaturated systems, following photo-oxidation. Charcoal is particularly resistant to photo-oxidation and consequently this material is concentrated during the procedure while other organic materials are oxidized and removed. The aryl and O-aryl regions of the CP/MAS spectrum only are used. If the O-aryl region shows the presence of lignin or lignin-like structures, then an area of 1.7 times the O-aryl region is subtracted from

[1] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

the aryl region to correct for any aryl C from noncharcoal materials. The corrected aryl area is then further corrected for the inefficiency of the CP to measure the highly unsaturated ring structures of the charcoal structure using the formula

$$f_a(\mathrm{CP}) = 0.27 \times f_a/(1 - f_a + 0.27 \times f_a) \qquad [1]$$

From the measured CP/MAS aryl signal (f_a[CP]) the corrected f_a can be calculated (Skjemstad et al., 1999). For the group of soils analyzed here, no lignin correction was required. Some organic materials which are highly physically protected within the <53-μm aggregates can also survive this treatment through protection from the uv radiation or the activated oxygen. For this reason, only the aryl region was used and a correction for CP inefficiency also needed to be made.

Chemical Analyses

Soil pH

Soil pH was determined in a 1:2 soil/water solution using a VIT90 Video Titrator (Radiometer Analytical A/S, 1989).

Organic Carbon

Total OC was determined using a LECO high-temperature C analyzer (Merry and Spouncer, 1988). Carbonate-C was determined volumetrically by calcimeter (Loveday and Reeve, 1974) and organic C (OC) estimated by difference. Organic C in <53-μm suspensions was determined by an externally heated chromic acid procedure (Heanes, 1984).

Total Nitrogen

Total soil N concentrations were determined with a LECO CN-2000 Dumas dry combustion procedure (Laboratory Equipment Corporation, 1994).

RESULTS

Some chemical, physical, and mineralogical data for the five soils are given in Table 1. Samples from each of the soils were separated into <53- and >53-μm fractions and the former subjected to 2 h of photo-oxidation. The organic C contents of the soils and each of the fractions are given in Table 2. Similar proportions of the TOC were present in the <53-μm fractions (77–88%) but the recovery of OC following photo-oxidation was more variable (13–41%).

To ascertain the general chemical nature of the OC in the soils and fractions following photo-oxidation, solid-state ^{13}C CP/MAS NMR spectra of the samples were obtained. The spectra for each of the five soils and their corresponding <53-μm fractions following photo-oxidation are shown in Fig. 1. The contribution of each of these regions from the soil before separation and the <53-μm fractions following photo-oxidation are given in Fig. 2. The <53-μm fractions were corrected for loss of OC resulting from photo-oxidation (Table 2).

For the Brennyville soil, the aryl-C was reduced by separation and photo-oxidation to ~25% of the original level. For the Vallers and Walla Walla soils, the aryl-C was reduced to ~75% of the original while the Elliott and Houston Black were reduced to near 50%. Charcoal content of the soils was calculated using the NMR data from the photo-oxidized fractions and is presented in Table 2. Charcoal represents between 1.8 and 13.6 g C kg^{-1} of soil or between 10 and 35% of the soil TOC.

Table 2. Total Organic C (TOC) in soils, fractions, and the charcoal C content. Values in parentheses represent the percentage contribution of that fraction to the TOC of the soil.

Soil series name	TOC	OC† in <53-μm fractions	OC in <53-μm fractions after photo-oxidation	Charcoal C
	g C kg^{-1} soil			
Brennyville silt loam	18.6	14.3 (77)	2.5 (13)	1.8 (10)
Elliott silt loam	28.7	25.0 (87)	8.4 (29)	6.6 (23)
Houston Black clay	36.9	30.0 (81)	10.4 (28)	7.6 (21)
Vallers silty clay loam	41.3	36.3 (88)	16.4 (40)	13.6 (33)
Walla Walla silt loam	10.3	8.2 (80)	4.2 (41)	3.6 (35)

† Organic C.

As further evidence that most of the material remaining after photo-oxidation was indeed charcoal, samples of the <53-μm fractions from the Elliott and Vallers soils following photo-oxidation and HF treatment were studied by SEM. Electron micrographs of charcoal particles showing blocky but plant-like characteristics are shown in Fig. 3. The elemental composition of these particles was determined by EDX analyzer and shown not to be of mineral origin.

DISCUSSION

The CP/MAS NMR spectra obtained from the five soils are typical of those reported in the literature for soils after HF treatment showing distinct peaks attributable to alkyl, O-alkyl, aryl, O-aryl, carbonyl, and ketone/aldehyde structures (Skjemstad et al., 1994a; Skjemstad et al., 1996; Schmidt et al., 1999). Although the various functional groups are reported in grams of C per 100 g of TOC (Fig. 2), it is recognized that the CP/MAS technique is not quantitative for soil organic C. As demonstrated by Skjemstad et al. (1996, 1999), the aryl charcoal fraction can be seriously underestimated by CP/MAS and a Bloch decay experiment is required to estimate charcoal-C accurately. The data in Fig. 2 therefore are not correct but indicate the relative changes in functional groups. For charcoal-C calculations, a Bloch decay correction is made on the aryl-C fraction following photo-oxidation. The application of this correction was discussed in detail by Skjemstad et al. (1999).

Photo-oxidation greatly decreased the levels of carbonyl-, O-aryl-, O-alkyl-, and alkyl-C but the impact on aryl-C, although decreased in all cases, was more variable. As demonstrated by Skjemstad et al. (1996), natural soil organic matter was rapidly oxidized by photo-oxidation with the exception of charcoal that was highly resistant to the process. The major reasons for the variable recovery of aryl-C were because of the levels of lignin removed in >53-μm fractions as well as the lignin, tannin, and lignin breakdown products oxidized in the <53-μm fractions. It was also likely that a small fraction of the charcoal materials, particularly those of small particle size, were also oxidized by the photo-oxidation

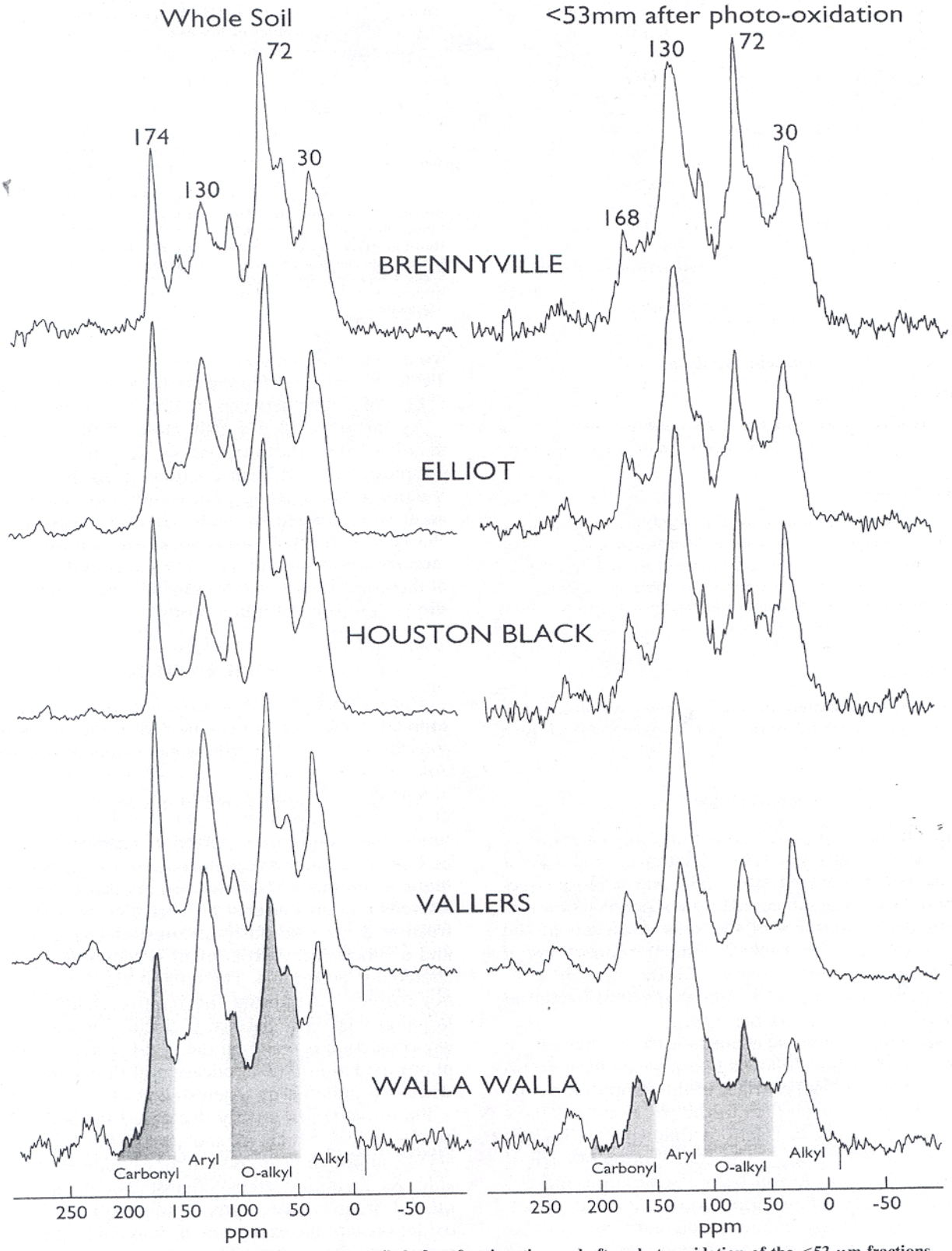

Fig. 1. Nuclear magnetic resonance spectra of the five soils before fractionation and after photo-oxidation of the <53-μm fractions.

procedure since smaller pieces of charcoal were not entirely inert to the process. The photo-oxidation technique appeared to effectively concentrate the aryl charcoal fraction however. For example, the aryl-C region in the Brennyville soil showed a high O-aryl signal near 150 ppm compared with the aryl-C signal near 130 ppm (Fig. 1). There was also evidence of a small signal near 120 ppm on the side of the larger aryl-C signal. These peaks are characteristic of lignin (Maciel et al., 1981) and indicate that the aryl-C in the sample was largely

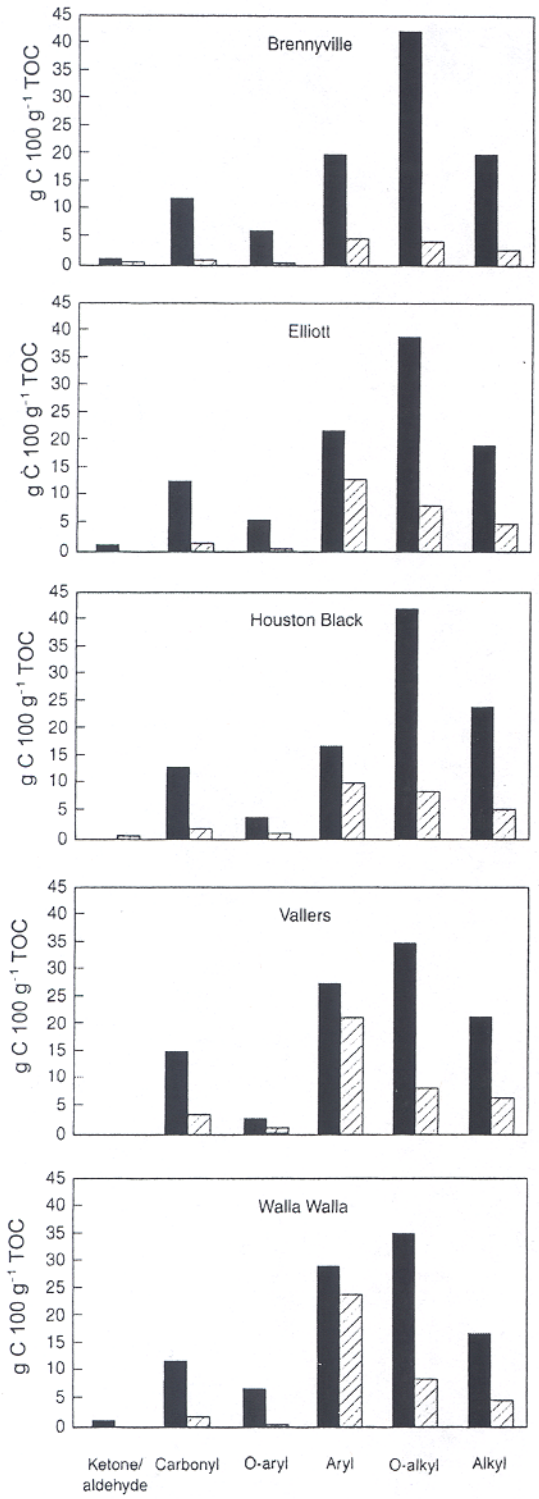

Fig. 2. The relative proportions of C in six functional regions, expressed in grams of C per 100 grams of total organic C (TOC), in the original soil (black), and in the <53-μm fractions (hatched) after photo-oxidation as determined by solid-state ^{13}C cross-polarization magic-angle spin nuclear magnectic resonance (CPMAS NMR) spectroscopy.

lignin or lignin-like material. The Vallers sample on the other hand showed a large aryl-C peak with no distinct peaks near 150 or 120 ppm. The aryl profile was typical of charcoal materials as confirmed by the high recovery of aryl-C following photo-oxidation and again with no distinct peaks near 150 or 120 ppm. The aryl-C remaining following photo-oxidation was then used to calculate the charcoal content (Skjemstad et al., 1999) of the soils as reported in Table 2. It appears that charcoal can constitute a significant proportion of U.S. soils being as high as 13.6 g charcoal C kg^{-1} soil (Vallers) or as high as 35% of the TOC (Walla Walla), similar to Australian soils (Skjemstad et al., 1999).

The morphology of the charcoal particles was very similar to those reported by Skjemstad et al. (1996) for Australian soils, showing angular blocky particles with plant-like cellular characteristics. The origin of these charcoal materials is not clear since charcoal formed from agricultural burning cannot be distinguished from relic charcoal which may have persisted in the soil environment for hundreds or perhaps thousands of years.

The five soils reported in this study all contained measurable amounts of charcoal C ranging from 10 to 35% of the TOC or 1.8 to 13.6 g charcoal C kg^{-1} soil. This charcoal must be considered as representing a soil organic pool highly resistant to biological oxidation. Albrecht et al. (1995) found that C added as burned stubble did not support microbial respiration. The ash C, chemically different from the C in wheat straw, was not available as energy for soil organisms. Current soil testing laboratory analyses detect and report the C in burned material as "soil organic matter" even though remains of the burned stubble are biologically inactive. Skjemstad and Taylor (1999) showed that even the Walkley and Black (1934) chromic acid oxidation method without external heating could not effectively discriminate between soil charcoal and other soil organic C forms. This suggests that traditional methods for estimating soil organic matter may severely overestimate the fraction of soil organic matter that might be available to microbial decomposition, even under intensive tillage regimes, and results from these methods must be interpreted with caution.

Incorporation of organic residues into soils rather than removal or burning can result in improved aggregate stability from increased formation of polysaccharide (Lynch and Bragg, 1985) and other binding agents (Muneer and Oades, 1989a,b; Capriel et al., 1990). The role of charcoal is much less clear. Glaser et al. (2000) found that black C in a Brazilian soil represented up to 45% of the total C. They postulated that slow oxidation of side chains in black C creates carboxylic groups that increases cation-exchange capacity and maintains soil organic matter stability. Skjemstad et al. (1996) also reported significant amounts of carbonyl-C, probably present as carboxyl groups, associated with finely divided charcoal particles separated from soil but could not be certain that these groups were not formed during the photo-oxidation procedure. More recently, Smernik et al. (2000) using the NMR technique of proton spin relaxation editing, showed that the charcoal in soils contained considerable carbonyl functionality possibly resulting from in situ weathering. Similarly, the NMR spectra from the <53-μm fractions following photo-oxidation given in Fig. 1, also showed appreciable carbonyl-C

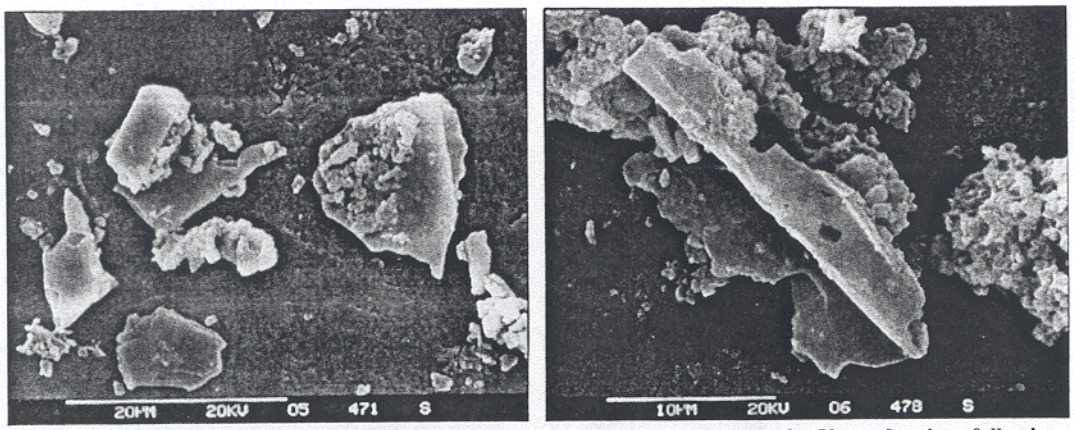

Fig. 3. Scanning electron microscopy photos: (a) Elliott silt loam and (b) Vallers silty clay loam of <53-µm fractions following photo-oxidation and HF treatment. Blocky, plant-like particles with fractured edges are characteristics of finely divided soil charcoal fragments.

signal near 168 ppm, which is characteristic of an aryl-C substituted with a carboxyl group. These groups may play a role in soil structural stability through cation bridging with clays but the absolute amounts of these groups in the soils were small (Fig. 2) and it is unlikely that they play a significant role in soil aggregate formation and structural resilience in clay soils.

Of the five soils used in this study, three contain significant quantities of charcoal (>5 g C kg^{-1} soil). For the past 5000 yr or so, these soils have been under prairie or oak (Quercus L.) savannah vegetation (Anderson, 1990) where fire has been prevalent. Analysis of further soil samples from different geographic regions and with a history of different vegetation cover would help to identify the role of fire, particularly fire in prairie systems, in the production of significant quantities of charcoal and the capacity of soils to preserve this material over long periods of time.

SUMMARY

The increased interest in soil C sequestration and its impact on climate change requires a better understanding of the C dynamics in agricultural soil systems. This work characterized the OC and charcoal-C content in a few important agricultural soils in the U.S. The charcoal occurs in varying amounts and can be identified after photo-oxidation treatment. The charcoal was determined as a portion of the TOC and must be assumed to be highly resistant to microbial activity and further chemical decomposition. Charcoal can constitute a large proportion of recalcitrant C pools in agricultural soils and can greatly impact soil C dynamics (Skjemstad et al., 2001). The processes of charcoal formation, its biological, physical, and chemical properties and distribution in many soils are largely unknown and require further study. Understanding the role of charcoal in nutrient cycling and C sequestration is vital for understanding the role and minimizing the impact of agriculture on climate change.

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