

Note

Synthesis and characterisation of laboratory-charred grass straw (*Oryza sativa*) and chestnut wood (*Castanea sativa*) as reference materials for black carbon quantification

Karen Hammes^a, Ronald J. Smernik^b, Jan O. Skjemstad^c, Andreas Herzog^d,
Ulrich F. Vogt^d, Michael W.I. Schmidt^{a,*}

^a University of Zurich, Department of Geography, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

^b Soil and Land Systems, School of Earth and Environmental Sciences, University of Adelaide, Waite Campus, Urrbrae, SA 5064, Australia

^c CSIRO Land and Water, Glen Osmond, Australia

^d EMPA Materials Science and Technology, Laboratory for High Performance Ceramics, Ueberlandstrasse 129, CH-8600 Dübendorf, Switzerland

Received 1 March 2006; received in revised form 28 June 2006; accepted 4 July 2006

Available online 7 September 2006

Abstract

We synthesised large (~2 kg) quantities of two chars for use as commercially available reference materials for the quantification of black carbon (BC). We pyrolysed chestnut wood (*Castanea sativa*) and grass straw (*Oryza sativa*) at 450 °C under a N₂ atmosphere, which mimics the oxygen-free conditions on the inside of burning material at a moderate burning temperature. The charred materials were dominated by aromatic carbon (~70%), had low H/C (~0.7) and O/C (~0.3) ratios and low surface areas (2–6 m² g⁻¹). Isotopic changes on charring were small (≤0.3‰). In these respects, the synthesised chars were similar to chars produced at low temperature (<500 °C) in natural fires and thus may prove to be appropriate materials for calibrating BC quantification methods. Both chars have been used in a comparative study of BC quantification.

© 2006 Elsevier Ltd. All rights reserved.

1. Introduction

Methods that can reliably quantify BC in various matrices are needed to provide more accurate global carbon budget assessments, air pollution inventories and fire history reconstructions (Kuhlbusch, 1998). The development and testing of BC quantification

methods would benefit from well characterised char reference materials, to aid in the understanding of the disparate results obtained from different quantification methods (Schmidt et al., 2003). While soot (formed at higher temperature) is commercially available as a reference material, char from low temperature natural biomass burning is not. For this purpose we synthesised chars at 450 °C, a typical temperature for natural fires (Turney et al., 2006) and covering the lower temperature end of BC production. Producing the chars under exact laboratory

* Corresponding author. Fax: +41 44 635 6848.

E-mail address: mschmidt@geo.unizh.ch (M.W.I. Schmidt).

conditions ensures that these materials can be reproduced in the future. To our knowledge this is the first detailed characterisation of wood and grass char produced specifically for use as BC reference materials. They are available from our laboratory. They have been used in a comparative study of BC quantification (<http://www.geo.unizh.ch/phys/bc>).

In this study, we (1) provide detailed characterisation of two chars produced under controlled conditions, (2) compare them with other artificial and natural chars (where burning conditions are often unknown) and (3) assess their suitability as reference materials.

2. Experimental

The chestnut wood (*Castanea sativa*) originated from a single tree in a forest in southern Switzerland (Ticino, between Bedano and Gorduno, 530 masl). The grass straw (*Oryza sativa* L. cv Arborio) also originated from southern Switzerland (Ticino, between Locarno and Ascona, 197 masl) from a commercial rice farm (Terreni alla Maggia SA, CH-6612 Ascona). The materials were not further dried before charring. Debarked and cut chestnut wood (40 × 5 × 5 cm) and bundled grass straw were charred in a GERO GLO 40/11 pyrolysis oven (Neuhausen, Germany; 0.8 m × 0.31 m diameter), under a N₂ atmosphere (flow 500 L h⁻¹). The temperature was raised from room temperature to 200 °C (300 K h⁻¹) and then to 450 °C (50 K h⁻¹), at which it was held for 5 h to achieve a constant weight. The charcoal was collected after cooling (8 h), crushed in a mechanical crusher and milled in a ball mill to a fine powder. The material was stored in a cool, dry place in aluminium containers. Samples were weighed before and after pyrolysis to determine mass loss. The ash content was determined using the loss on ignition (LOI) method where samples are dried at 105 °C for 24 h and ignited at 400 °C for 16 h.

Solid state ¹³C NMR spectra were obtained at a ¹³C frequency of 50.3 MHz with a Varian Unity 200 spectrometer using cross polarisation (CP) and Direct Polarisation (DP). Samples were spun at 5 kHz. For the CP spectra a 1 ms contact time was used. The recycle delay was 4 s for the uncharred samples and 1 s for the charred samples; 1000 scans were collected for the uncharred samples and 4000 for the charred samples. For the DP spectra a total of 1000 scans was collected with a recycle delay of 90 s. Chemical shifts were externally refer-

enced to the methyl resonance of hexamethylbenzene at 17.36 ppm.

Stable carbon isotope ($\delta^{13}\text{C}$) values were determined by Iso-Analytical Ltd. (Sandbach, UK) using a Europa Scientific 20–20 isotopic ratio mass spectrometer (EA-IRMS). Total C, H and N analysis for calculation of H/C and O/C molar ratios were carried out with a LECO CHN-900 instrument and O analysis with a LECO RO-478 instrument.

Nitrogen adsorption surface area measurements were performed at 77 K after drying (200 °C, 1 h) using a SA 3100 analyser (Coulter, USA). The apparent nitrogen surface area was calculated using the BET equation for a pressure range p/p_0 0.0033 – 0.1.

3. Results and discussion

3.1. Characterisation of wood and grass char materials

The H/C and O/C ratios of the wood and grass decreased on charring, as reported in previous studies in which biomass (peas, peat and sapwood) was subjected to different degrees of heating (Baldock and Smernik, 2002; Almendros et al., 2003; Braadbaart et al., 2004). A van Krevelen plot of H/C versus O/C (Fig. 1) is a convenient way to visualising the changes. Three steps are characteristic of condensation to form a carbon-rich product: (1) initial dehydration; (2) dehydrogenation and demethylation (loss of CH₃); (3) decarboxylation (loss of CO₂) and demethylation (see insert in Fig. 1; Bal-

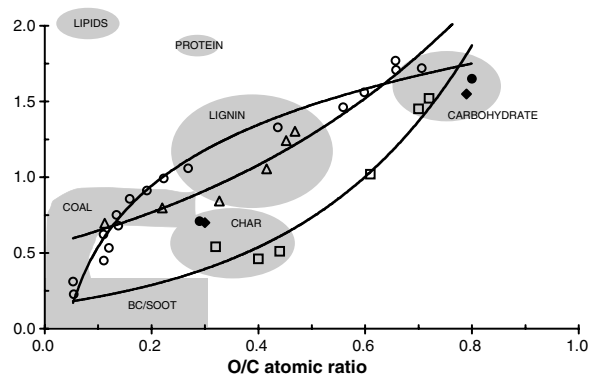


Fig. 1. Processes related to charring of biomass: wood (filled diamonds) and grass straw (filled circles), before and after charring. Heating of other biomass materials: peas (open circles, Braadbaart et al., 2004), peat (open triangles, Almendros et al., 2003) and sapwood (open squares, Baldock and Smernik, 2002). Grey shadings = areas of biomolecular components (adapted from Kim et al., 2003).

dock and Smernik, 2002; Kim et al., 2003; Braadbaart et al., 2004). The H/C and O/C ratios of the wood and grass char were almost identical. However, we suspect that the grass char (and grass straw) picked up some water, increasing the H/C and O/C ratios. Generally, H/C and O/C ratios of chars differ, depending on the type of material, the heating atmosphere and temperature of formation (intensity of heating) as illustrated by the different charred biomass in Fig. 1.

Carbon-13 CP and DP MAS NMR spectra are shown in Fig. 2. Only CP spectra were recorded for the uncharred materials since the CP “observability” for the wood and grass was 99% and 93% respectively. The distribution of signals in the spectra are presented in Table 1. The spectra of both the wood and the grass before charring were dominated by signals in the O-alkyl C region (45–110 ppm), reflecting the dominance of cellulose (Preston et al., 1998; Baldock and Smernik, 2002). A methoxyl carbon signal at 56 ppm and several signals in the aryl C region (165–110 ppm) were stronger for the wood than for the grass, reflecting a higher content of lignin and/or presence of hydrolysable tannin in the wood. Weak signals were present in the alkyl (0–45 ppm) and carboxyl (210–165 ppm) regions.

The CP and DP spectra of both materials after charring were similar, being dominated by peaks

in the aryl region (110–165 ppm). The aryl peak was centred at 126.5 ppm in the CP spectrum and 127.3 ppm in the DP spectrum for the wood char, and at 128.8 ppm in the CP spectrum and 129.3 ppm in the DP spectrum for the grass char. Both chars contained 10–15% of the signal in each of the alkyl (0–45 ppm) and O-alkyl (45–110 ppm) regions (Table 1), indicating that not all the C was transformed into condensed aryl structures. However, it should be noted that around half of this signal could be attributed to signal from the aromatic spinning sidebands. The DP “observability” for the wood char was 88% and for the grass char 82%, while the CP “observability” was 24% and 40% respectively.

Both char spectra contained shoulders in the O-aryl region (160 ppm), which might be attributable to remaining lignin structures, or newly formed compounds, such as benzo-furans, polycyclic aromatic hydrocarbons or heterocyclic compounds (Baldock and Smernik, 2002). The small peak at 168 ppm in the grass char spectrum could indicate the presence of small amounts of carboxylic acid (attached to aryl rings) or bicarbonate in the alkaline ash.

The ash content was much less for wood ($\sim 1 \text{ g kg}^{-1}$) than for grass (77 g kg^{-1} , Table 1), as expected (Krull et al., 2003). Mass recovery (wood

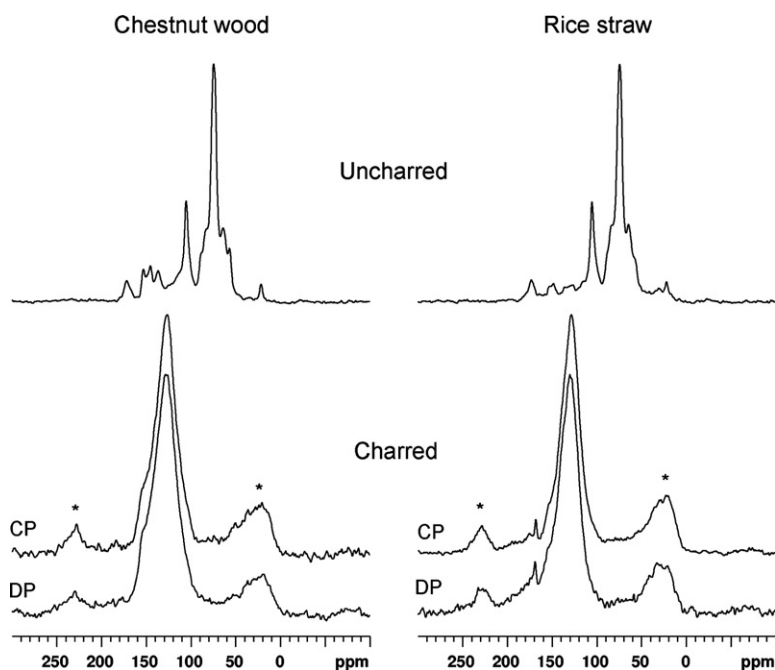


Fig. 2. ^{13}C NMR CP and DP spectra of wood and grass straw, before and after charring; * indicates spinning sidebands.

Table 1
Isotopic, elemental composition and CP and DP NMR signal intensities of wood and grass before and after charring ($n = 1-2$)

Reference material	Mass (%) ^a	C (g kg ⁻¹)	N (g kg ⁻¹)	H (g kg ⁻¹)	O (g kg ⁻¹)	Atomic ratio		Mass ratio	$\delta^{13}\text{C}$ (‰(V-PBD))	Mineral matter ^b (g kg ⁻¹)	BET surface area (m ² g ⁻¹)	% Total acquired NMR signal (ppm)							
						H/C	O/C					C/N	Carboxyl C (210–165 ppm)	Aryl C (165–110 ppm)	O/N-Alkyl C (110–45 ppm)	Alkyl C (45–0 ppm)	CP	DP	CP
Wood		457.7	0.7	59.4	479.7	1.6	0.8	920	-26.6	0.8	-		3.8	-	21.8	-	72.8	1.7	-
Wood char		682.0	1.6	39.8	270.6	0.7	0.3	690	-26.9	0.5	2.0		2.7	4.2	74.4	76.6	13.1	12.1	9.8
Recovery (%)	40	59	98	27	23														
Grass		422.7	6.2	58.7	452.9	1.7	0.8	64	-26.4	76.8	-		4.9	-	13.6	-	75.6	-	5.9
Grass char		586.3	12.4	34.7	227.0	0.7	0.3	49	-26.5	191.5	5.9		5.5	9.3	71.7	73.9	11.2	8.3	11.5
Recovery (%)	35	49	71	21	18														

^a Mass recovery after pyrolysis in mass%.

^b Mineral matter (ash) determined by LOI.

40%, grass 35%) were similar to those previously reported for pyrolysis residues formed at 450–480 °C under an inert atmosphere (mass recovery 20–30%; Czimczik et al., 2002; Brown et al., 2006). Recovery of initial carbon was 49% for grass and 59% for wood after pyrolysis. Due to the preferential loss of H and O with heating, carbon concentration and degree of aromatisation typically increased with pyrolysis. Mass recovery of the initial nitrogen was 71% for grass and 98% for wood (Table 1). This is consistent with decreasing C/N ratio values on charring, indicating that nitrogen is preferentially preserved (Almendros et al., 2003).

Stable C isotope ratio values for the chestnut wood (-26.6‰) and grass (-26.4‰) were typical for many C₃ plants (Krull et al., 2003), with minor depletion ($\leq 0.3\%$) on charring (Table 1). Isotopic depletion in ¹³C also took place in other wood types after heating to temperatures between 150 °C and 480 °C (Czimczik et al., 2002; Turney et al., 2006).

The surface area of the chars (< 10 m² g⁻¹) was similar to that found for pitch pine char produced at a final temperature of 450 °C, and less than that produced at higher temperature (> 500 °C, 250–340 m² g⁻¹; Brown et al., 2006).

3.2. Comparison with other laboratory-produced and natural chars

Several studies report laboratory-produced char, but only a few report elemental (H, C, N, O) concentrations and specific surface area (no isotopic ($\delta^{13}\text{C}$) information) for the same samples (11 out of 44 individual chars) formed between 70 and 1000 °C (Baldock and Smernik, 2002; Czimczik et al., 2002; Nguyen et al., 2004; Zhu et al., 2005; Brown et al., 2006; Turney et al., 2006). The final formation temperature and gas composition during heating influence char properties (Brown et al., 2006). For natural chars, the temperature of formation is difficult to measure and is rarely known. Thus, parameters like H/C ratio, specific surface area and $\delta^{13}\text{C}$ value could help infer the temperature of formation of natural chars. Interestingly, an H/C atomic ratio > 0.5 seems to indicate chars which experienced temperatures < 500 °C, whereas chars with H/C < 0.5 were mostly formed at higher temperature (500–1000 °C). Additionally, these low temperature chars generally had low surface area (< 25 m² g⁻¹), whereas high temperature chars generally had large surface area (214–336 m² g⁻¹), except

when temperature ramping was slow ($< 0.5 \text{ m}^2 \text{ g}^{-1}$, $30\text{--}200 \text{ }^\circ\text{C h}^{-1}$). Low temperature chars also had a high surface area when exposed to oxygen during heating, compared to an inert atmosphere.

Our lab-produced chars have characteristic low H/C ratios, small surface areas and no significant isotopic depletion on charring, typical of low temperature fires ($400\text{--}500 \text{ }^\circ\text{C}$). They also represent BC-rich materials formed at a lower temperature than soot, which normally forms $> 500 \text{ }^\circ\text{C}$ and so contribute to the span of BC-rich materials that can be used as reference materials for analysis. By analysing the above characteristics for natural chars, it may become possible to estimate a burning temperature range for chars. Interestingly, the few natural chars analysed for H/C, specific surface area and $\delta^{13}\text{C}$ value, so far display characteristics of high temperature burning. It could be that (1) natural fires do not form much char, due to the presence of oxygen and the preferential formation of ash, or (2) low temperature chars actually form but transport and subsequent storage in soil and sediment selectively preserve the chemically more resistant high temperature chars.

To summarise, the lab-produced wood and grass char analysed here (1) represent typical low temperature chars, according to elemental composition H/C, $\delta^{13}\text{C}$ value and surface area and (2) can be reproduced, so they can be used as reference materials to calibrate BC methods for comparative studies.

Acknowledgements

Michael Schneider (ETH) performed the elemental analysis. The BC steering committee (M.W.I. Schmidt, C.A. Masiello, J.O. Skjemstad, D.M. Smith, L.A. Currie) initiated a project to study reference materials for black carbon analysis. We thank two anonymous reviewers for constructive comments.

Associate Editor—Sylvie Derenne

References

- Almendros, G., Knicker, H., Gonzalez-Vila, F.J., 2003. Rearrangement of carbon and nitrogen forms in peat after progressive thermal oxidation as determined by solid-state ^{13}C - and ^{15}N -NMR spectroscopy. *Organic Geochemistry* 34, 1559–1568.
- Baldock, J.A., Smernik, R.J., 2002. Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. *Organic Geochemistry* 33, 1093–1109.
- Braadbaart, F., Boon, J.J., Veld, H., David, P., Van Bergen, P.F., 2004. Laboratory simulations of the transformation of peas as a result of heat treatment: changes of the physical and chemical properties. *Journal of Archaeological Science* 31, 821–833.
- Brown, R.A., Kercher, A.K., Nguyen, T.H., Nagle, D.C., Ball, W.P., 2006. Production and characterization of synthetic wood chars for use as surrogates for natural sorbents. *Organic Geochemistry* 37, 321–333.
- Czimczik, C.I., Preston, C.M., Schmidt, M.W.I., Werner, R.A., Schulze, E.-D., 2002. Effect of charring on mass, organic carbon, and stable carbon isotope composition of wood. *Organic Geochemistry* 33, 1207–1223.
- Kim, S., Kramer, R.W., Hatcher, P.G., 2003. Graphical method for analysis of ultrahigh-resolution broadband mass spectra of natural organic matter, the Van Krevelen diagram. *Analytical Chemistry* 75, 5336–5344.
- Krull, E.S., Skjemstad, J.O., Graetz, D., Grice, K., Dunning, W., Cook, G., Parr, J.F., 2003. ^{13}C -depleted charcoal from C_4 grasses and the role of occluded carbon in phytoliths. *Organic Geochemistry* 34, 1337–1352.
- Kuhlbusch, T.A.J., 1998. Black carbon and the carbon cycle. *Science* 280, 1903–1904.
- Nguyen, T.H., Brown, R.A., Ball, W.P., 2004. An evaluation of thermal resistance as a measure of black carbon content in diesel soot, wood char, and sediment. *Organic Geochemistry* 35, 217–234.
- Preston, C.M., Trofymow, J.A., Niu, J., Fyfe, C.A., 1998. ^{13}C CPMAS-NMR spectroscopy and chemical analysis of coarse woody debris in coastal forests of Vancouver Island. *Forest Ecology and Management* 111, 51–68.
- Schmidt, M.W.I., Masiello, C.A., Skjemstad, J.O., 2003. Final recommendations for reference materials in black carbon analysis. *EOS* 84, 582–583.
- Turney, C.S.M., Wheeler, D., Chivas, A.R., 2006. Carbon isotopic fractionation in wood during carbonization. *Geochimica et Cosmochimica Acta* 70, 960–964.
- Zhu, D., Kwon, S., Pignatello, J.J., 2005. Adsorption of single-ring organic compounds to wood charcoals prepared under different thermochemical conditions. *Environmental Science and Technology* 39, 3990–3998.