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A demonstration of the high variability of chars produced from wood in bushfires

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ABSTRACT

Vegetation fires play a major role in global C cycling through the addition of inert carbon (char) to the environment. The objective of this study was to compare and contrast the chemical composition of 53 natural chars collected from the soil surface 6–32 years after a natural fire. In order to achieve this, we applied a recently developed nuclear magnetic resonance (NMR) technique that gauges the degree of condensation of aromatic structures within chars. Our results show that the degree of condensation varied considerably among char samples ($n = 4–5$), collected from burnt-out tree stumps at each of the 11 fire sites. This demonstrates that there is a great degree of variability in the composition of the char produced in natural fires, which is likely to be reflected in widely varying rates of char decomposition. This highlights a major difficulty in quantifying the effects of vegetation fires on global C cycling. Importantly, no differences could be discerned between chars of different ages, indicating that ageing of this type of char in this environment is slow on the decadal timescale. Finally, this study demonstrates that although char samples appear to preserve a record of fire conditions, great care must be taken when interpreting this record to account for the high degree of heterogeneity in char composition. Bulking of char samples would alleviate this problem to some extent; however, bulking would mask the inter-particle heterogeneity clearly evident in this study.

1. Introduction

Char, produced through the incomplete combustion of plant biomass and litter during natural vegetation fires (variously referred to as bushfires or wildfires), has been identified as an important component of the stable soil organic pool and thus plays an important role in the global carbon cycle (Kuhlbusch and Crutzen, 1995; Masiello and Druffel, 1998; Schmidt and Noack, 2000). The size of the global stable C pool represented by char is critically dependent on both the rate at which char is produced and the rate at which it decomposes, both of which are difficult to estimate.

Widely varying estimates of annual global char production have been reported. Earlier studies suggested that biomass burning, on a global basis, produces 500–1700 Tg of char per year (Seiler and Crutzen, 1980). More recent calculations estimate worldwide char formation from biomass burning to range from 40–241 Tg/year, with as much as 80% of this remaining as residues in and on soil (Kuhlbusch, 1998; Schmidt and Noack, 2000; Forbes et al., 2006).

Estimating the rates of char decomposition is difficult for three main reasons: (1) Char is very stable and decomposition of char is generally slow. Only a small proportion of char C is mineralized over common research timeframes (<5 years) (Shindo, 1991; Baldock and Smernik, 2002; Hamer et al., 2004; Liang et al., 2008). As a result, estimates of rates of char decomposition can be compromised by the presence of small amounts of more readily mineralized non-char material that is attached or adsorbed to the char. (2) Char mineralization rates vary depending on the environmental conditions (Cheng et al., 2008b). (3) Char is not a homogenous material but rather a "spectrum" (Hammes et al., 2007) of carbon materials that will vary in their susceptibility to decomposition. Therefore, a prerequisite to obtaining accurate estimates of char decomposition rates is to be able to identify the types of char produced in vegetation fires and how they change over time.

Fires occur in both grassland and forest ecosystems and char residues from these different vegetation types have been found to be chemically different in several ways, including in their susceptibility to microbial degradation (Hamer et al., 2004; Knicker et al., 2008; Hilscher et al., 2009; Nguyen and Lehmann, 2009). Furthermore, the highly variable nature of natural fires produces char with a variable degree of charring. In general, the concentration of oxygen at the time of burning determines whether flaming or smouldering conditions develop and this influences mass loss, C loss, aromatic C content and the isotopic composition of the residue char (Krull et al., 2003; Alexis et al., 2010). There is some evidence that size fractions of char have characteristically distinct compositions, with larger char particles having more aromatic C and being less reactive to oxidation than smaller particles, suggesting that finer particles will be mineralized more rapidly than coarser char particles (Rumpel et al., 2007; Nocentini et al., 2010).

Further, understanding of the heterogeneous nature of chars produced during vegetation fires requires the application of

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techniques specifically designed to be sensitive to structural differences. Recently we have developed a simple and rapid technique for measuring aromatic condensation of chars, based on the change in the ^{13}C NMR chemical shift of benzene when it is sorbed to char (McBeath and Smernik, 2009; McBeath et al., 2011). This technique clearly showed that aromatic condensation steadily increased with increasing temperature across a thermosequence of chars produced from chestnut wood in the laboratory at temperatures between 200 °C and 1000 °C (McBeath et al., 2011).

This study uses the same method to characterize one class of char produced in typical (non-catastrophic) vegetation fires and its variability over space and time. The aims of this study are: (1) to assess the variability of the most recalcitrant chars produced in forest fires by analysing 4–5 samples from 11 different sites; and (2) to seek information about the degree of ageing that char may undergo on a decadal timescale by comparing chars that have been subjected to environmental conditions for 6–32 years.

2. Materials and methods

2.1. Study site and sampling

Char samples were collected in 2010 from 11 sites in the southern Mount Lofty Ranges, approximately 15 km east of Adelaide, South Australia. All sites were within four bushland parks: two sites were within Belair National Park (35°0′47″S, 138°39′21″E), four sites were within Black Hill Conservation Park (34°52′29″S, 138°43′17″E), two sites were within Mark Oliphant Conservation Park (35°01′57.90″S, 138°42′19.23″E) and three sites were within Scott Creek Conservation Park (35°05′20.87″S, 138°41′38.58″E). These parks contain a range of vegetation types including sclerophyll woodlands, open and grassy woodlands and grasslands. The woodlands are dominated by different species of *Eucalyptus* (Paton et al., 2000) and the grasslands are dominated by species of *Austrostipa* and *Austrodanthonia* (Poaceae), and *Lomandra* (Liliaceae) (Moore, 1970). The climate is Mediterranean, i.e. characterized by hot dry summers and cool, wet winters. Most fires occur in the summer and have both anthropogenic and natural causes.

Detailed fire records of last fire year were obtained from the Department of Environment and Heritage, South Australia and fire maps were used to identify sampling sites (see Supplementary material, S1a–S1d). The year of the most recent fire at each site was determined to have occurred between 1978 and 2004, as detailed in Table 1. Several char samples were collected from various burnt-out tree stumps at each site. Sampling was restricted in this way to restrict sample heterogeneity by targeting chars exposed to the hottest temperatures and longest heating times and to obtain chars that are most resistant to decomposition. A selection of 4–5 different sampled chars from each of the 11 sites was air dried for 24 h then gently ground to a coarse powder for analysis. Partially charred particles were not selected and char produced from grass biomass could not be identified at the sites used.

2.2. Elemental and isotopic analysis

Carbon content (%C) and carbon stable isotope ratios (δ^{13}C) were determined using an elemental analyser (Automated Nitrogen Carbon Analyser; ANCA-SL) interfaced with a SerCon 20–20 isotope ratio mass spectrometer (EA-IRMS). Samples were measured in duplicate and sample runs also included blanks and laboratory standards for calibration.

Table 1
Year of most recent fire year at each sampling site.

Site	Years
Belair National Park	1978, 2004
Black Hill Conservation Park	1978, 1994, 1998, 2004
Mark Oliphant Conservation Park	1994, 2004
Scott Creek Conservation Park	1978, 1984, 1988

2.3. Solid state ^{13}C CP NMR analysis

Solid state ^{13}C cross polarization (CP) NMR spectra were obtained at a frequency of 100.6 MHz using a Varian Unity INOVA 400 NMR spectrometer. Samples were packed in 7 mm diameter cylindrical zirconia rotors with Kel-F rotor end caps and spun at the “magic angle” (54.7°) at 6500 ± 100 Hz in a Doty Scientific supersonic MAS probe. Free induction decays (FIDs) were acquired with a sweep width of 50 kHz; 1216 data points were collected over an acquisition time of 15 ms. All spectra were zero filled to 8192 data points and processed with a 50 Hz Lorentzian line broadening and a 0.010 s Gaussian broadening. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm. Spectra represent the accumulation of 4000 scans and were acquired using a 90° ^{1}H pulse of 5–6 μs duration, a 1 ms contact time and a 1 s recycle delay. Spin counting was carried out using the method of Smernik and Oades (2000a,b). Glycine (AR grade, Ajax Chemicals) was used as the external reference for spin counting, i.e. the glycine spectrum was acquired separately to those of the samples.

2.4. Determination of aromatic condensation

Aromatic condensation of the chars was determined using the method of McBeath and Smernik (2009) and McBeath et al. (2011). Briefly, aliquots of each char sample (200 mg) were placed in 2 ml glass vials with PTFE lined screw caps. Neat $^{13}C_6$ labelled benzene (99% isotopic purity; ca. 10 μl) from Cambridge Isotope Laboratories, Inc. (Andover, Massachusetts), was added using a micropipette and the samples were shaken for 1 min and stored at room temperature until analyzed. Samples were analyzed using solid state ^{13}C CP NMR spectroscopy. Spectra were acquired using the same acquisition conditions described above but fewer scans (16–128) were required.

2.5. Statistical analysis

Analysis of variance (ANOVA) was undertaken using the Genstat® V.13 statistical package. The design used sample as a factor (representing each site-year sampling) with a block structure of replicates.

3. Results and discussion

3.1. Carbon content and stable isotope ratio

The carbon content of the chars ranged from 53–75% (Table 2). No consistent trend in carbon content was apparent, with variation between chars collected at a single site just as great as variation between sites. The δ^{13}C values of the chars ranged from −23.6‰ to −27.2‰. This is consistent with all chars being derived from woody plants, which use the Calvin–Benson (C_3) photosynthetic pathway.

3.2. Aromatic condensation of bushfire chars

The char samples were characterized using a novel nuclear magnetic resonance (NMR) method that gauges the degree of condensation of their aromatic structures (McBeath and Smernik, 2009; McBeath et al., 2011). In this technique, the chemical shift