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Rapid molecular screening of black carbon (biochar) thermosequences obtained from chestnut wood and rice straw: A pyrolysis-GC/MS study

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ABSTRACT

Rice straw and chestnut wood were heated between 200 and 1000 °C (T_{CHAR}) to produce Black C 'thermosequences'. The molecular properties of the charred residues were assessed by pyrolysis-GC/MS to investigate the relation between charring intensity and pyrolysis fingerprint. Samples obtained at $T_{CHAR} > 500$ °C (wood) or >700 °C (straw) gave low quality pyrograms and poor reproducibility because of high thermal stability, but pyrolysis-GC/MS allowed to track the thermal degradation of the main biocomponents (polysaccharides, lignin, methylene chain-based aliphatics, triterpenoids, chlorophyll and proteins) in the lower temperature range, mostly occurring between T_{CHAR} 250 and 500 °C. With increasing T_{CHAR}, the charred residues of these biocomponents lose characteristic functional groups, aromatise and finally condense into non-pyrolysable biomass. The proportions of the pyrolysis products of unspecific origin (benzene, toluene, PAHs, etc.), increase with charring intensity, while the ratios that reflect the abundance of alkyl cross-linkages between aromatic moieties (e.g. benzene/toluene, naphthalene/alkylnaphthalene) decrease. These results provide the guidelines to using pyrolysis-GC/MS for the molecular characterisation of different components in Black C and biochar, which is an important parameter for predicting Black C/biochar behaviour in soil. Results are consistent with earlier studies of these samples using the BPCA (benzenepolycarboxylic acid) method and the ring current-induced ^{13}C benzene chemical shift NMR (Nuclear Magnetic Resonance) approach. Pyrolysis-GC/MS provides more information on molecular structures in the low temperature range ($T_{CHAR} \leq 500$ °C) while the BPCA and NMR ring current methods provide more reliable estimations of charring intensity, especially at higher temperatures ($T_{CHAR} \geq 500$ °C).

1. Introduction

Thermally modified biomass, i.e. Black C (BC) or biochar, is increasingly being amended to cultivated soil to enhance soil fertility, reduce soil degradation and mitigate greenhouse gas accumulation into the atmosphere through C sequestration [1–4]. Nonetheless, the behaviour of BC in the soil environment depends on a large array of intrinsic BC properties (e.g. feedstock characteristics, charring temperature and duration, particle size) and soil conditions (moisture content, pH,

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composition and activity of the microbial population, parent material, etc.), which are only superficially understood [5–13].

One of the key parameters in predicting BC degradation/preservation in soil is the degree of thermal alteration (charring intensity). Black C envelopes, with increasing charring intensity, weakly charred biomass, charcoal, soot and graphitic BC [14–16], which creates the so-called 'BC combustion continuum'. At the high-temperature end, BC consists of a strongly polycondensed (graphitic) aromatic network lacking most functional groups present in non-charred biomass. On the low temperature end, weakly charred biomass often contains chemical building blocks that reflect the biocomponent from which they originate, such as methoxyphenolic moieties from lignin and furan-like structures from carbohydrates [17–19]. As each biocomponent thermally rearranges at different temperatures, they form individual 'combustion continua'. As a result, recalcitrant and labile phases often coexist in a BC specimen [20]. Typically, with increasing charring intensity the C content, degree of condensation, specific surface area and sorption capacity of BC increase [21], while its susceptibility to degradation decreases [22–25].

Pyrolysis-GC/MS is one of the techniques available for studying the molecular properties of organic matter. It has been applied to BC previously [26–31], and the relationship between pyrolysis fingerprint and BC degradability was recently demonstrated by incubation studies [32,33]. Nonetheless, detailed interpretations of the data generated are scarce, especially using a relatively high pyrolysis temperature (700–750 °C) that is considered more suitable for BC [17,34,35]. The main objective of the present study is to (i) determine the thermal degradation of the compound groups present in lignocellulosic biomass (rice straw and chestnut wood) at temperatures that cover the range of both natural fires as well as common biochar preparation conditions (200–1000 °C). These feedstocks and corresponding chars were studied previously by the benzene polycarboxylic acid (BPCA) method [36] and solid-state ^{13}C Direct Polarisation Nuclear Magnetic Resonance (^{13}C DP NMR) in combination with polycondensed aromatic ring current-induced chemical shift modification of bound ^{13}C benzene ("ring current NMR") [37]. Moreover, rice straw-derived BC/biochar has a large potential for C sequestration in rice-based systems yet knowledge on its molecular properties is scarce [13,38,39]. The detailed description of the pyrolysis-GC/MS results aims to serve as a guideline for the assessment of the molecular properties of BC using this technique.

2. Materials and methods

Chestnut (*Castanea sativa*) wood and rice (*Oryza sativa* Arborio) straw chars were prepared according to the protocol described in Hammes et al. [40]. Debarked and cut biomass was placed in a Carbolite CTF 16/75 furnace under N_2 flow (13 L h^{-1}) and the temperature raised from room temperature to 200 °C at a rate of 300 °C h^{-1} and then to 250–1000 °C at a rate of 50 °C h^{-1} to produce the chestnut wood and rice straw thermosequences. The final temperature (T_{CHAR}) was held constant for 5 h to assure complete charring, followed by a cooling period of 8 h after which the charred residues were collected. Samples were weighed before and after heat treatment to determine mass loss. The thermosequences originally included reference wood and grass chars of the Black Carbon Steering Committee [41] obtained at 450 °C, which were described by Hammes et al. [40,42], and studied by [28] and [30] using pyrolysis-GC/MS. However, these reference materials produced disparate results in the thermosequence, probably due to differences in feedstock particle size ([36,43] this study), and the corresponding pyrolysis-GC/MS results are therefore provided as Supplementary Material (S1). Samples are referred to as WX00 (chestnut; wood chars) and GX00 (rice; grass chars), with X00 indicating T_{CHAR}. Table 1 provides mass recovery after charring and the elemental composition of the residues.

Work by Keiluweit et al. [44] showed that wood and grass feedstocks charred at 200 °C showed no chemical changes by FTIR and a weight loss of only 3%, and the cellulose remained virtually unaltered until 225 °C charring as detected by a wide array of methodologies including pyrolysis-GC/MS, suggesting that the G200 and W200 pyrolysates can be considered as representative of the feedstock.

Pyrolysis-GC/MS was performed according to Kaal et al. [34]. Briefly, 1–1.5 mg of sample was placed in fire-polished quartz tubes with quartz wool on both ends and pyrolysed using a CDS Pyroprobe 5000 Pt coil filament instrument for 10 s at 750 °C. Pyrolysis products were swept into a 6890N gas chromatograph (Agilent Technologies) by He flow (1 cm^3 min^{-1}), separated on a HP-5MS polysiloxane-based column (temperature program 50–325 °C at 20 °C min^{-1}) and identified using an Agilent 5975B mass spectrometer operating in 70 eV electron impact mode. Quantification of pyrolysis products was based on the peak area of dominant and/or characteristic fragment ions. The relative abundances of each pyrolysis product were calculated as the percentage of the sum of all peak areas (total quantified peak area, TQPA). This is a semi-quantitative exercise that allows better recognition of differences between samples than visual inspection of pyrograms alone. Supplementary Material (S1) contains the background dataset, including pyrolysis product identifications, corresponding ion fragments, retention times and the relative contributions (%TQPA).

3. Results and discussion

3.1. Pyrolysis-GC/MS

3.1.1. Total quantified peak area (TQPA)

The pyrolysis products quantified cover the major peaks in the pyrograms, which implies that TQPA provides a rough estimation of signal intensity. In the present study, signal intensity is controlled by the pyrolysability of the material analysed [45]. Because the signal intensity of the chestnut wood chars obtained at $T_{CHAR} \geq 600$ °C and rice straw chars at $T_{CHAR} \geq 800$ °C was too low for meaningful quantification, in combination with poor reproducibility, we report only the results for chars obtained at $T_{CHAR} \leq 500$ °C and ≤700 °C for chestnut wood and rice straw, respectively. Fig. 1 shows that there is an exponential decrease in signal intensity with