The analysis of benzene polycarboxylic acids (BPCA) as a quantitative measure for black carbon in soil samples is a well-established method. The oxidation of polycondensated black carbon molecules leads to the formation of BPCA, which subsequently can be quantified by gas chromatography with flame ionization detector (GC-FID). The relative contribution of the single acids to total BPCA-C depends on the cluster sizes of black carbon (i.e. degree of condensation and aromaticity of the chars) and therefore may represent changes in chemical quality. Hence, the BPCA method provides information about the source and the formation conditions of the char analysed. Here, we tested if the BPCA patterns reflect the maximum temperature experienced by laboratory produced wood char.

Small wood chips of chestnut hardwood (Castanea sativa) were pyrolysed at maximum temperatures between 250 and 1000 °C under constant N2 stream. The maximum temperatures were held constant for 5 hours. The chars were then characterised using the BPCA method to trace changes in individual BPCA contribution (B3CA, B4CA, B5CA, B6CA) to the total content. Further, the samples were analysed for BET-N2 specific surface area, char colour and elemental composition (CHNO).

Increasing temperatures led to a preferential loss of H and O due to dehydration, demethylation and decarboxylation upon charring. Further, we observed decreasing C/N rations with increasing temperatures, a result of a strong N enrichment following charring at elevated temperatures. Our results show consistently increasing proportions of B6CA (mellitic acid) over the whole temperature range reflecting an increasing degree of condensation.

The results of this study stress the suitability of the BPCA molecular marker technique as the basis for a quality index in order to characterize chars from different sources and to improve our understanding of biochar properties as related to their formation conditions.

Characterisation of biochar by cryo-focusing, double-shot Py-GC-MS

S. Kimber[1], L. Van Zwieten[1], E. Berger[1], S. Joseph[2] A. Hosaka[3], C. Watanabe[3], A. Downie[4]

[1]NSW Department of Primary Industries, Wollongbar NSW, Australia;
[2]School of Material Science and Engineering, University of NSW, Australia;
[3]Frontier Laboratories Ltd., Fukushima, Japan;
[4]Best Energies Pty Ltd, Somersby, Australia.

Research has shown that the properties of biochar vary significantly with feedstock and processing conditions. Rapid and accessible technologies are needed for the characterisation of biochars to predict their agronomic and environmental value.

Analytical Double shot, cryo-focusing pyrolysis coupled with GC-MS offers a rapid and inexpensive tool for the assessment of the suitability of biochars for agricultural / forestry use. We have tested numerous biochars produced by BEST Energies, and tracked changes to the biochars following incubation in soils

An initial thermal desorption allows the quantitation and identification of volatile components including bio-oils. Bio-oils may have either a positive or negative effect on plant growth. Following thermal desorption, flash pyrolysis provides structural information on the "stable" carbon component of the biochar.

Increasing awareness of the potential value of biochar in Australia has led to a situation where demand far out-strips supply. Consequently, individuals are attempting back yard production, or imports from Asia and the sub-continent. The likely agronomic value of these chars is an unknown quantity, and indeed, a standard for the classification of biochar per se does not exist. We are proposing to utilize this analytical methodology to test the suitability of biochars for field application.

This paper will present data on the calibration of the cryo-focusing technique to establish bio-oil content in a number of biochar samples. Further data will be presented on the characterisation of carbon fractions in soils (both control soils and following biochar addition).

This technique is also currently being calibrated against a number of conventional methodologies including solid state nuclear magnetic resonance (SS-NMR), mid-infra red reflectance spectroscopy (MIR), and electron microscopy including x-ray diffraction (XRD). Calibrations are being made with pure biochar, soils and soils amended with biochar. Studies on some Australian Aboriginal midden soils have also been undertaken, the topic of another abstract.

Poster Presentations

B1: Chemical oxidation of Eucalyptus benthamii charcoal

C.F. Alho[1], E.H. Novotny[2], C.M. de Freitas Maia[3], E.A. de Lima[3], F.A. Hansel[3]

[1]Department of Soil, Universidade Federal Rural do Rio de Janeiro, Seropédica, Brazil;
[2]Embrapa Solos, Rio de Janeiro, Brazil,
[3]Embrapa Florestas, Colombo, Brazil

The charcoal presents a condensed aromatic structure that guarantees its recalcitrant nature, being an efficient material for sequestering organic carbon in soils. However, charcoal does not present satisfactory functional groups, important for its reactivity and contribution for the soil cation exchange capacity. Its application upon soil, and consequent biological and chemical alterations, will generate those functional groups, however that process can take decades. In this context, preliminary studies indicate that it is possible to promote those chemical alterations by chemical (acid oxidation), biological or enzymatic pathways. Charcoal has been used to increase crop yields and productivity, to reduce greenhouse gases emission (CO^2, CH4 and specially N2O) and the need for fertilizer inputs. The aim of this study was to promote the chemical oxidation of Eucalyptus benthamii charcoal, intending the formation of functional groups attached to the charcoal's condensed aromatic structure. The charcoals were prepared using the conventional pyrolysis method (carbonization) at 500°C for 2 hours. The mean yield of charcoal, pyrolysis liquor and gases were 36.42%, 33.75% 29.83%, respectively. The charcoals were submitted to four treatments (T1, T2, T3 e T4) using 2g of powdered charcoal (<0.05 mm) and 20 ml solution. The different solutions used were: T1 - H2O2 5% and H3PO4 0.1 mol.L 1; T2 - HNO3 5% and H3PO4 0.1 mol.L 1; T3 - H2O2 2.5% and HNO3 2.5%; T4 - H3PO4 85%. The four treatments were heated at 70°C for 2 hours using a block digester. The characterization and efficiency of each treatment, concerning to its chemical alterations, were evaluate using ¬¬¬solid state ^{13}C Nuclear Magnetic Resonance.

Acknowledge: The authors are grateful to the Irish Research Council for Science, Engineering and Technology (IRCSET – Ireland) and National Counsel of Technology and Science Development (CNPq – Brazil) for the financial support.