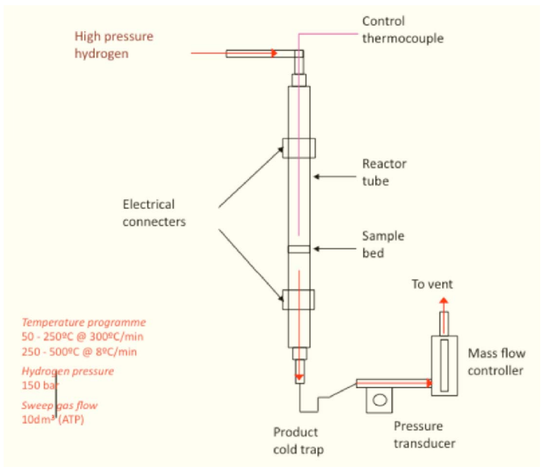
Biochar determination by hydrogen pyrolysis (hypy)

Philippa Ascough (1), Michael Bird (2*), William Meredith (3), and Colin Snape (3)
(1) SUERC, Glasgow,UK; (2) James Cook University, Cairns (3) University of Nottingham, Nottingham, UK;
* presenting author (michael.bird@jcu.edu.au)

Introduction

- pyrogenic carbon (biochar) is an important source of environmental/chronological information and well as having application in soil amelioration, carbon sequestration and energy generation
- a requirement for all of the above is the ability to reliably quantify biochar and this has remained a difficult task, with a range of methods used with varying success
- Ideally a method for PC quantification should rapidly, cheaply and unambiguously, isolate a consistent, stable component of biochar for analysis



lab-scale hypy rig - currently three in the world, one at Nottingham, one at JCU, one in China

Hydrogen pyrolysis

- hypy was developed for converting coal to liquid and gaseous products and involves pyrolysis (at up to ~600˚C) assisted by high hydrogen pressures (>10 MPa) in the presence of a dispersed sulphided molybdenum catalyst.
- the product of hypy is dichloromethane-soluble oil and gases such as methone
- previous work has demonstrated:

(i) 100% conversion lignocellulosic materials virtually 100% conversion of immature type Iand type II kerogens

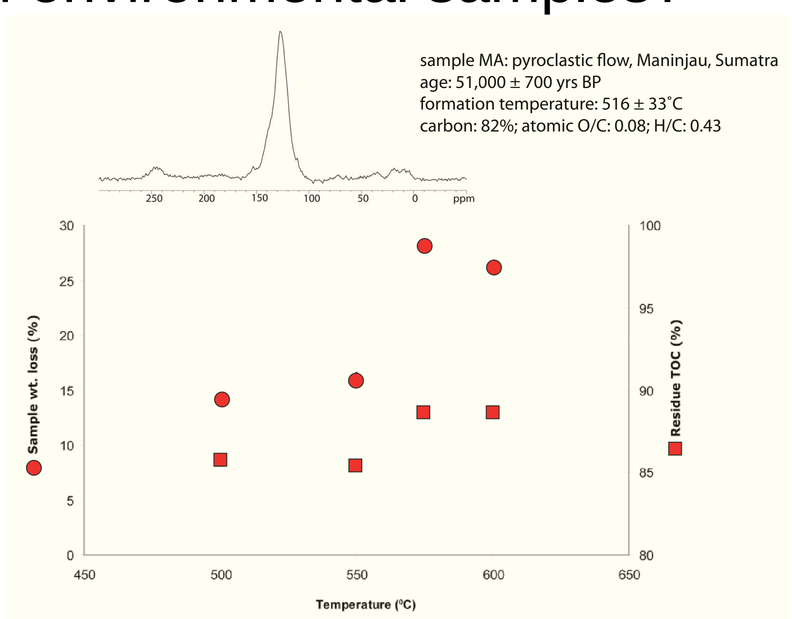
(ii) variable conversion for bituminous coals, with vitrinite and liptinite converted, leaving inertinite intact (which is biochar in coal petrology)

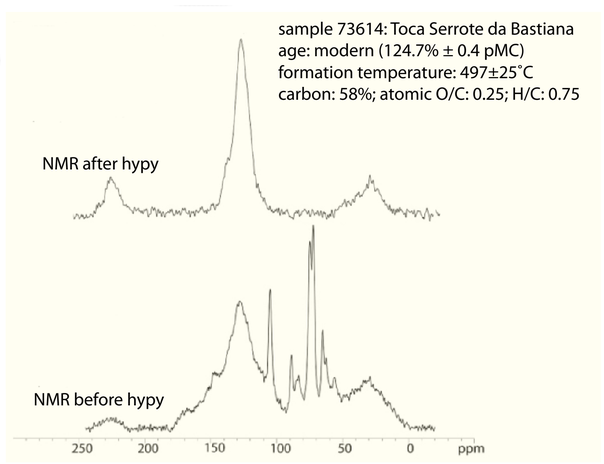
Can laboratory-scale hypy quantify biochar in environmental samples?

hypy of ‘good biochar’

- hypy of a biochar known from NMR to be dominantly composed of polycyclic aromatics resulted in 14-16% mass loss at 500-550˚C.
- %C increased from 81% initially to 85-86% at 500-550˚C
- small mass loss was mostly due to loss of water and replacement of oxygen by hydrogen (O/C 0.03) but a small amount of tar collected
- tar probably derived from highly aromatic humic acids also present in the sample? Beyond 550˚C hydrogasification to methane occurs

conclusion: hypy has minimal effect on resistant biochar





hypy of ‘bad biochar’

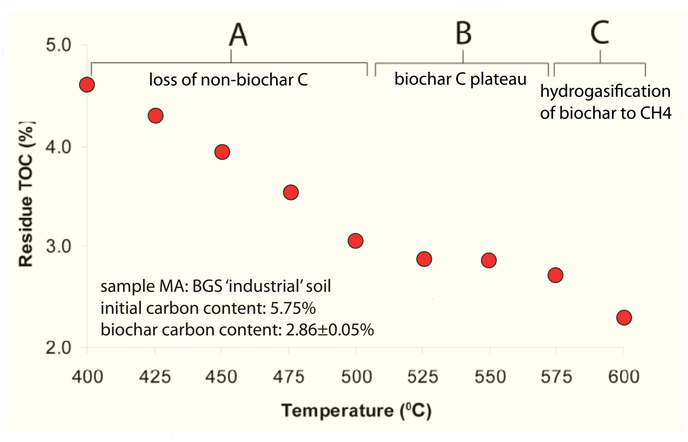
- hypy of a biochar known from NMR initially composed of a range of compounds removed all but the aromatic component of the sample

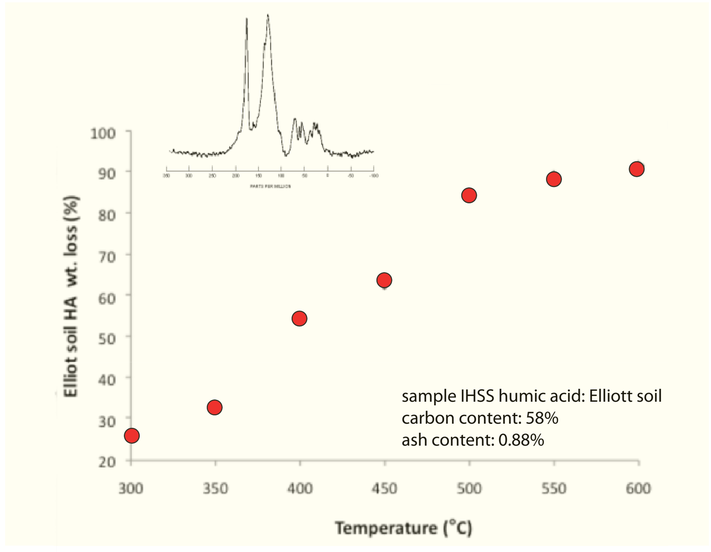
conclusion: hypy can effectively remove the labile components of biochar.

hypy of soil

- successive increases in hypy temperature on separate aliquots of the same soil show removal or progressively more carbon to ~500˚C, followed by a ‘plateau’ to 575˚C, corresponding to biochar carbon (temperature control is ±5˚C, so a large plateau).
- triplicate measurements suggest uncertainty of ±3%

conclusion: hypy can quantify biochar in complex environmental matrices





hypy of humic acid

- hypy of an IHSS humic acid standard indicates only 85-90% removal by 500˚C
- this HA is derived from a burnt prairie soil and is rich in aromatic compounds

conclusion: some of this humic acid is of biochar origin

conclusions

- hypy potentially provides a rapid (15 minute), cheap (US$10) and reliable technique for (i) quantifying the resistant component of biochar in complex matrices including soils as well as marine and terrestrial sedimentary records, (ii) decontaminating biochar for radiocarbon dating, and (III) isolating the ‘non-biochar’ components for further chemical characterization

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for further information see: Ascough, P. L, Bird, M. I., Meredith, W., Snape, C. E, Vane, C., Brock, F., and Higham, T. (2009) Hydropyrolysis as a tool for enhanced 14C age measurement and quantification of Black Carbon in depositional environments. Quaternary Geochronology, 4, 140-147.