

Aromatic Condensation of Black Carbon: Its measurement and importance

A thesis submitted to the University of Adelaide
in fulfilment of the requirements for the degree of Doctor of Philosophy

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March 2012

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ABSTRACT

Black carbon (BC) is an important constituent of soils and sediments due to its role in a range of biogeochemical processes. However, since BC represents a continuum of materials with no clear-cut boundaries, it is challenging to identify and quantify. This limits our understanding of its contribution to terrestrial, marine and atmospheric carbon cycles and the role it plays in influencing climate.

The focus of this study was on first improving and refining a novel solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopic that offers great potential for the characterisation of BC. Once optimised, this technique was applied to a variety of BC samples in order to address some key questions in BC science.

The technique developed here is a simple and rapid method for gauging the degree of aromatic condensation of chars, a molecular-scale property that affects both their degradability and sorption affinity. The foundation for the technique has been described previously. Its basis is the effect that “ring currents” that are induced in aromatic structures have on the ^{13}C NMR chemical shift of probe molecules when sorbed to the char. The improvement in the technique described here involves a direct addition of the probe molecule ($^{13}\text{C}_6$ -benzene) directly to the dry char. This is demonstrated to be a much more efficient method of loading the probe molecule, both in terms of the amount of expensive ^{13}C -labelled compound require and also in the time required for sample preparation and NMR acquisition.

Following the optimisation of the ring current method, it was applied to three sample sets of BC materials to address in detail three important aspects of BC composition: (i) the effect of temperature on BC; (ii) the effect of feedstock on BC; and (iii) the nature and variability of charcoal produced in natural fires.

The parameter derived from the ring current technique, $\Delta\delta$, was demonstrated to be a good measure of aromatic condensation. This was most evident for a thermosequence of twelve chestnut wood chars produced at temperatures from 200 to 1000°C, as it clearly captured the variations in char composition with increasing temperature. Through the use of the ring current method that it became clear that there are two distinct phases in charcoal formation: first an increase in aromaticity, and second a structural rearrangement creating condensed aromatic structures.

The use of different feedstock resulted in critical differences in aromatic condensation between biochars produced at the same temperature. In particular, feedstocks with higher lignin contents, such as woody materials, were found to form more condensed aromatic structures with a higher degree of aromaticity compared to biochars from mineral-rich feedstocks (e.g. crop residues) and waste materials (e.g. manures, food waste and papermill waste).

Lastly, the variability in chars produced in natural vegetation fires was gauged through the analysis of 53 natural chars collected from the soil surface six to thirty years after natural fires. The aromatic condensation was found to vary considerably among 4-5 char samples collected at each of the fire sites, despite efforts to sample only the most carbonized char from burnt-out tree stumps. This demonstrates that there is great degree of variability in the composition of the char produced in such fires, which is likely to be reflected in widely varying rates of char decomposition.

DECLARATION

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution to Ashlea Doolette and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

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Anna McBeath

Date

ACKNOWLEDGEMENTS

I am heartily grateful to my supervisors, Ronald Smernik and Evelyn Krull, whose encouragement, guidance and support from the beginning to end enabled me to develop an understanding of all things black carbon and the opportunity to travel the world!

I would also like to thank Michael Schmidt and his team in the Soil Biogeochemistry group at the University of Zurich for hosting me and giving me the opportunity to collaborate with some of the brightest minds and build my networks.

I would like to acknowledge for the generous financial support of Future Farming Industries CRC, AUGU/RC Heddle Fund, AW Howard Memorial Award, Australian Geographic Society, Adelaide Research Abroad Sponsorship and the Australian Society of Soil Science Inc. Without this financial support I wouldn't have had the opportunity to venture beyond Adelaide to make some incredible collaborations around the world.

To my sister, Therese who seems to have all the answers to my most difficult problems, be it scientific or life, thank you!

To my friends and family thank you for your support and understanding for my need to pursue a greater understanding of all things unknown.

Lastly to my Lucas, thank you for the sacrifice you have made so that I may fulfil my dreams and for your unconditional support, love and confidence in me.

PUBLICATIONS ARISING FROM THIS THESIS

Smernik R.J. and McBeath A.V. 2009. A simple method for determining biochar condensation. Oral presentation at: *1st Asian Pacific Biochar Conference*, Gold Coast, Australia.

McBeath A.V. and Smernik R.J. 2009. Measuring the black carbon continuum- a new method for identifying black carbon in the environment. Oral presentation at: *European Geosciences Union General Assembly*, Vienna, Austria.

McBeath A.V. and Smernik R.J. 2009. Variation in the degree of aromatic condensation of chars. *Organic Geochemistry* 40:1161-1168.

McBeath A.V., Smernik R.J., Schneider P.W., Schmidt M.W. and Lehman J. 2010. Aromatic condensation as a measure of black carbon stability: A NMR study. Poster presentation at: *Organic Matter Stabilization and Ecosystem Functions*, Presquile de Giens, France.

McBeath, A.V., Smernik, R.J., Schneider, M.P.W., Schmidt, M.W.I. and Plant, E.L., 2011. Determination of the aromaticity and the degree of aromatic condensation of a thermosequence of wood charcoal using NMR. *Organic Geochemistry* 42, 1194-1202.

McBeath A.V., Smernik R.J. and Krull E.S. 2011. Assessing changes in environmental charcoal over a 30 year period as a way to predict decadal ageing of biochar. Oral presentation at: *2nd Asian Pacific Biochar Conference*, Kyoto, Japan.

McBeath A.V. 2011. Biochar- an initiative for humanity's environmental future. Oral presentation at: *C9-Go8 HDR Forum: Clean Energy and Global Change for the Future*, Tsinghua University, Beijing, China.

McBeath A.V., Smernik R.J., Krull E.S. and Lehman J. (submitted). The influence of feedstock and production temperature on biochar chemistry: An NMR study. *Journal of Environmental Quality*.

STRUCTURE OF THIS THESIS

This thesis is presented as a combination of papers that have been published, have been submitted for publication or have been prepared for submission.

Chapter 1 provides an overview of the literature on the chemical and physical nature and dynamics of black carbon in the soil environment. It will also discuss the current challenges facing the quantification of black carbon and how this relates to its heterogeneous nature in soil environments. This chapter includes the proposed objective of this research. Introductory material relevant to the published and submitted papers is not presented in detail in the literature review because it appears in the introduction of each chapter.

Chapter 2 comprises a paper published in *Organic Geochemistry*. It describes the modification of a novel method to measure the variation in the degree of aromatic condensation of chars using ^{13}C NMR spectroscopy.

Chapter 3 comprises a paper published in *Organic Geochemistry*. It provides validation of the novel technique developed in chapter 2 and describes the chemical changes at the molecular level in charcoal formation with increasing temperature.

Chapter 4 comprises a paper that has been submitted to the *Journal of Environmental Quality*. It describes how feedstock and temperature affects the aromaticity and aromatic condensation properties of biochar.

Chapter 5 comprises a paper that has been prepared for submission to *Organic Geochemistry*, it has not been submitted. It examines the effects of bushfire on char formation and describes the variation within the recalcitrant structures of environmental chars.

Chapter 6 provides a synthesis of the findings contained in this thesis and includes recommendation for future research.