12th Asia-Pacific Conference on Combustion,
Fukuoka International Congress Center, Fukuoka, Japan
1st -5th July 2019.

Exploring the properties of pyrogenic carbon with solid state ^{13}C nuclear magnetic resonant spectroscopy: a combustion wind tunnel study

N. C. Surawski[1, *], L. M. Macdonald[2], J. A. Baldock[2,] A. L. Sullivan[3], S. H. Roxburgh[3], P. J. Polglase[3, †]

[1]School of Civil and Environmental Engineering, University of Technology Sydney

81 Broadway, Sydney, 2007, Australia

[2]CSIRO Agriculture and Food

Locked Bag 2, Adelaide, South Australia, 5064, Australia

[3]CSIRO Land and Water

GPO Box 1700, Canberra, Australian Capital Territory, 2601, Australia

[†]Current address: School of Ecosystem and Forest Sciences

The University of Melbourne, Melbourne, Victoria, 3010, Australia

Abstract

Increasing the production of aryl carbon from wildland fire may be beneficial since it can be stored in soils for long periods of time rather than being emitted to the atmosphere or stored in soils in a less recalcitrant form. In this study, solid state ^{13}C nuclear magnetic resonant spectroscopy is used to explore the properties of pyrogenic carbon produced by fires burning with different fire spread modes. Forest litter fuels were burnt using in a combustion wind tunnel using a replicated experimental design. Experiments were performed with three different fire spread modes, involving heading fires that spread with the wind, backing fires that spread against the wind and flanking fires that spread perpendicular to the wind. Results show that heading fires produce significantly more aryl carbon than flanking fires. Analysis of the results with principal component analysis show that maximising the residence time of high temperature combustion and the combustion factor could be an effective method for increasing the production of aryl carbon from fire.

1. Introduction

Even though wildland fire is a necessary disturbance for the maintenance of some ecosystems [1], it has a range of negative impacts such as damage to assets and infrastructure, loss of life and impacts on climate and air quality [2, 3]. The most recent version of the Global Fire Emissions Database [4] suggests that wildland fire emits 2.2×10^{15} grams of carbon per year, averaged of the period from 1997-2016, which represents approximately 23% of annual anthropogenic carbon emissions from fossil fuel combustion and industrial sources. [5]. Apart from the release of carbon emissions to the atmosphere, it is important to consider the production of Pyrogenic Carbon (PyC) that is not emitted to the atmosphere to perform effective carbon budgets from wildland fire. This is the case since PyC is a potential carbon sink that involves carbon storage for long periods of time in soils [6,7].

Prescribed burning operations involve intentionally lit fires that are commonly undertaken in forested landscapes to protect against the deleterious aspects of unplanned wildfire [8]. While prescribed fires are often undertaken to protect against fire hazards associated with elevated fuel loads, here we focus on how prescribed burning operations could be modified to improve the overall carbon budget. A striking feature of prescribed burning operations is the range of ignition methods used to allow the burn objectives to be met [9, 10]. Previous research [11-13] has indicated that backing fires (i.e. fires that spread against the wind) and flanking fires (i.e. fires that spread perpendicular to the wind) burn more cleanly (i.e. with lower carbon monoxide emissions) and with a higher combustion efficiency compared to heading fires that spread in the direction of the wind. Based on these observations, the objective of this study is to explore whether the properties of PyC change with different fires spread modes with ^{13}C nuclear magnetic resonant spectroscopy (^{13}C NMR).

2. Methodology

2.1 Overview of experiments

A detailed overview of the fuel collection and handling methods and design of the fire behavior experiment can be found in Surawski et al. [14]. Here we focus on the aspects of the experiment relevant for investigating PyC. Experiments were performed in the Commonwealth Industrial Research Organisation (CSIRO) Pyrotron (Fig. 1), which is a combustion wind tunnel facility designed for investigating the behaviour, emissions and suppression characteristics of fires. Experimental fires were conducted with three fire spread modes (Fig. 2) that propagated with different directions relative to the prevailing wind. After the completion of experimental fires, PyC was sorted into four burnt fuel fractions consisting of partially burnt leaves, twigs and bark as well as an ash fraction. PyC samples were collected from three experimental fires for each fire spread mode.

---

* Corresponding author: +61 2 9514 9063
E-mail address: nicholas.surawski@uts.edu.au

Figure 1: Panoramic view of the CSIRO Pyrotron.

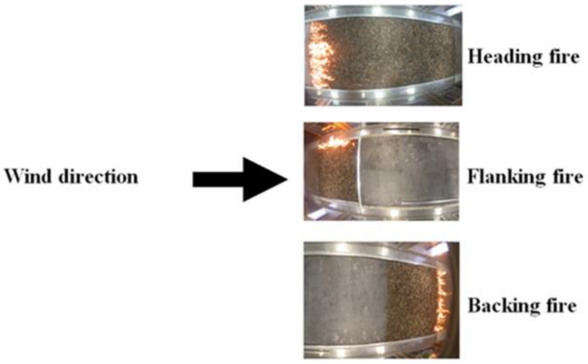

Figure 2: A schematic overview of the fire spread modes employed in this study.

2.2 Overview of ^{13}C NMR analysis

PyC was ground prior to solid state ^{13}C NMR analysis. Weighed samples (100–600 mg) with known carbon contents were packed into 7-mm-diameter zirconia rotors with Kel-F® end caps and spun at 5 kHz. Kel-F inserts were used to fill any gaps and place the sample in the middle of the rotor when samples did not fill the rotor completely. ^{13}C NMR spectra were acquired on a 200 Avance spectrometer (Bruker Corporation, Billerica, MA, USA) equipped with a 4.7 T, wide-bore superconducting magnet operating at a resonance frequency of 50.33 MHz. Chemical shift values were calibrated to the methyl resonance of hexamethylbenzene at 17.36 ppm, and a Lorentzian line broadening of 50 Hz was applied to all spectra.

2.3 Overview of statistical analysis

One Way Analysis of Variance was performed for PyC samples to test whether ^{13}C NMR spectral composition depended on FSM. Tukey Honest Significant Difference tests were used to assess the statistical significance for all pairwise comparisons. A 5% level for statistical significance was used.

Principal Component Analysis (PCA; [14]) was performed to explore the relationship between the ^{13}C NMR functional groups present in fuel samples burnt with different FSMs as well as their relationship with recorded fire behaviour variables. PCA was performed in using the FactoMineR package [15]. All data were centred and standardised with unit variance before analysis. Two Principal Components (PCs) were retained in all analyses due to 80% of the total variance being explained in all cases except one. The factoextra package was used to visualise [16], with PCA biplots being used to show both scores and loadings from the analysis. All statistical analyses were performed with RStudio Version 1.1.456.

3. Results

Figure 3 displays a summary of key results from the ^{13}C NMR analysis. This includes summary data for the integrated spectra as well as the percentage change in carbon composition through the application of different fires spread modes. For unburnt fuels, statistically significant differences in alkyl and O-alkyl carbon were found for all three vegetation components. Statistically significant differences in aryl carbon were found when comparing leaves and bark and twigs and bark. For di-O-alkyl carbon, statistically significant differences were found for leaves compared to bark and twigs to leaves. The only statistically significant result for burnt fuels was an increase in aryl carbon for ash from heading fires compared to flanking fires. No other burnt fuels yielded statistically significant differences in terms of the measured carbon functional groups.

Figure 4 shows the relationship between PyC samples, their ^{13}C NMR composition and the measured fire behaviour variables. Before presenting the results though, a few features inherent to the PCA biplot are worth noting. An attractive feature of the PCA biplot entails its ability to capture information from the scores and loadings matrices in the one plot [17]. Since PCA involves projecting a higher dimensional space to one of lower dimensionality, observations are mapped and stored in a new co-ordinate space in the scores matrix. In contrast, the loadings matrix captures the contribution of the original variable to a particular PC. In the PCA biplot, correlated variables (or observations) lie roughly parallel with each other (± 45 °), anti-correlated variables (or observations) lie roughly opposite one another (135-225 °) and un-correlated variables (or observations) are roughly orthogonal (45-135 °). Further, the length of an arrow indicates the degree of variability of a variable, with longer arrows indicating more variable data. Finally, observations that are found further from the origin in the PCA biplot indicate that the variable is strongly associated with that particular PC.

In Figure 4, there are four main clusters. In the top right quadrant, we see that two of the temperature residence times (i.e. time above 500 and 750 ° C; but not 250 ° C), maximum temperature, combustion factor and fuel moisture content are associated with the aryl carbon functional group. In the top left quadrant, the duration of flaming combustion and the time above 250 ° C are associated. In the bottom left quadrant, the N-alkyl, O-alkyl and di-O-alkyl functional groups are roughly parallel and point in the opposite direction of the aryl and O-aryl functional groups. In the bottom right quadrant, the duration of smouldering combustion, Byram fireline intensity, rate of spread, and ΔCO/ΔCO2 emissions ratio are all roughly parallel.

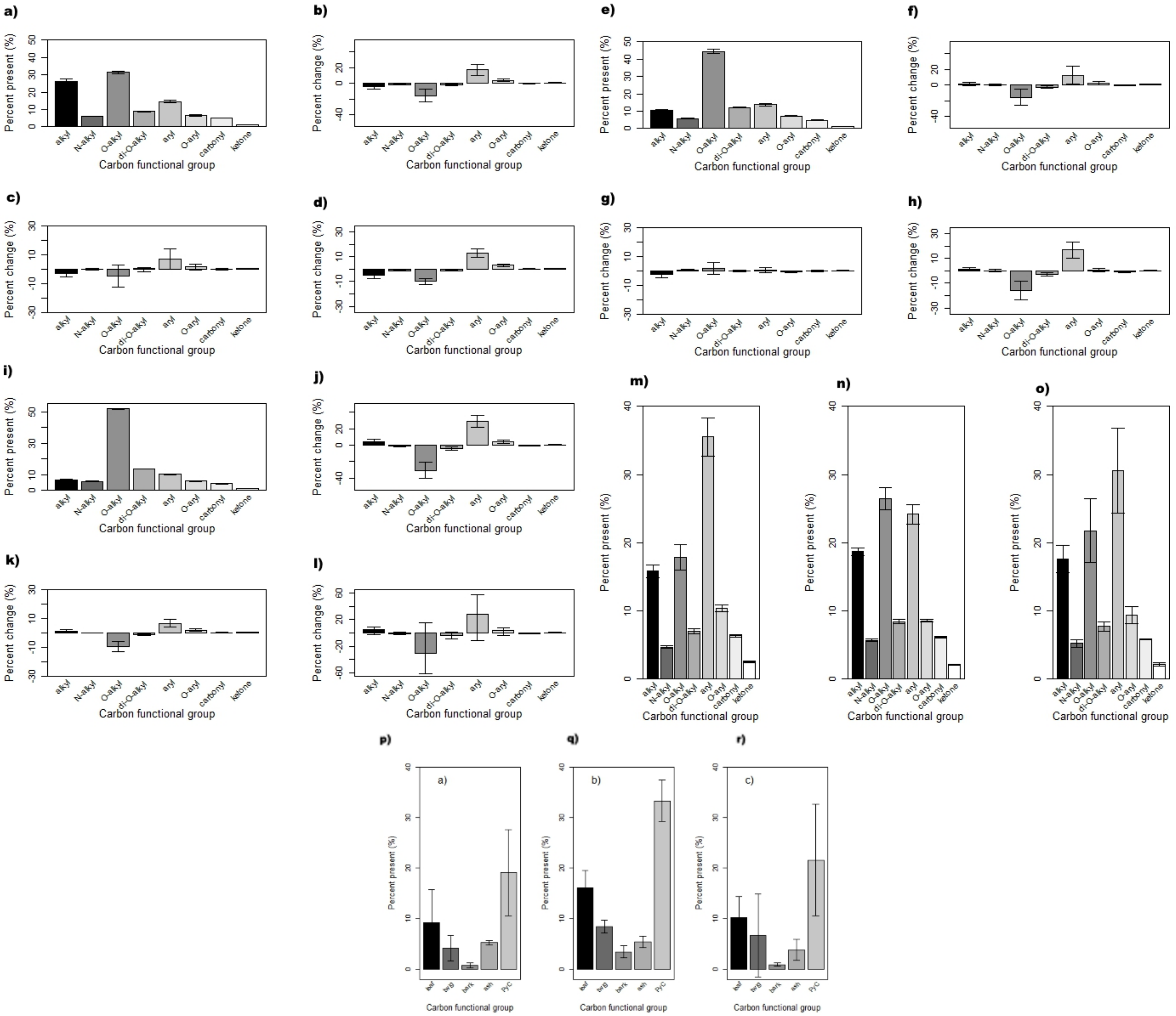

Figure 3: Graphical summary of the integrated ^{13}C NMR results for different carbon functional groups. Error bars in all panels are based on the standard deviation based on triplicate sampling. a) ^{13}C NMR composition for unburnt leaves. b) Percentage change in ^{13}C NMR composition for leaves burnt by heading fires. c) Percentage change in ^{13}C NMR composition for leaves burnt by flanking fires. d) Percentage change in ^{13}C NMR composition for leaves burnt by backing fires. e) ^{13}C NMR composition for unburnt twigs. f) Percentage change in ^{13}C NMR composition for twigs burnt by heading fires. g) Percentage change in ^{13}C NMR composition for twigs burnt by flanking fires. h) Percentage change in ^{13}C NMR composition for twigs burnt by backing fires. i) ^{13}C NMR composition for unburnt bark. j) Percentage change in ^{13}C NMR composition for bark burnt by heading fires. k) Percentage change in ^{13}C NMR composition for bark burnt by flanking fires. l) Percentage change in ^{13}C NMR composition for bark burnt by backing fires. m) ^{13}C NMR composition of ash from heading fires. n) ^{13}C NMR composition of ash from flanking fires. o) ^{13}C NMR composition of ash from backing fires. p) PyC for heading fires expressed as percentages of partially burnt leaves, twigs and bark as well as ash. q) PyC for flanking fires expressed as percentages of partially burnt leaves, twigs and bark as well as ash. r) PyC for backing fires expressed as percentages of partially burnt leaves, twigs and bark as well as ash.

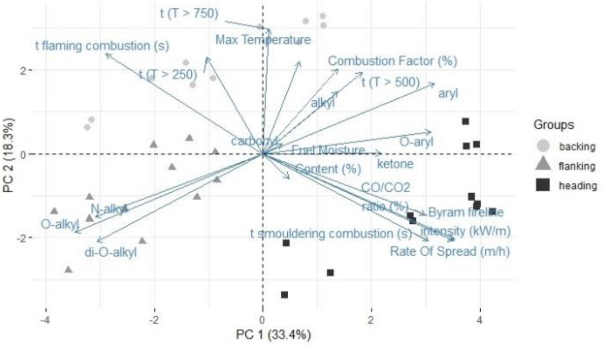

Figure 4: PCA biplot showing the relationship between a range of fire behaviour variables and 13C NMR composition for different fire spread modes. The percentage of variance accounted for by each principal component is displayed on each axis.

4. Discussion

Statistical testing of the differences in ^{13}C NMR composition showed that aryl carbon present in ash was higher for heading fires compared to flanking fires. All other tests for statistical significance for burnt fuels were insignificant. This may be considered a surprising result since insights from the thermokinetics of biomass combustion suggest that fire behaviour, including the influence of FSM, has the potential to alter the type of PyC that is not emitted to the atmosphere after fire [18-20]. Ball et al. (2004) proposed a model whereby flame dynamics act as a thermochemical oscillator with combustion periodically switching between the production of volatiles and that of char. When applied to a propagating fire, available evidence suggests that the combustion pathways associated with heading fire combustion would be directed towards the production of volatiles while preferential formation of char would occur from backing as well as flanking fires. Based on the current experiments, there does not appear to be very strong empirical support for the hypothesis that FSM affects the type of carbon functional groups present in PyC.

Having said that, the results (Figure 4) indicate how aryl carbon could be produced with different fire spread modes. In particular, increasing the temperature residence time as well as the combustion factor both appear to be valid mechanism for increasing aryl carbon production. In terms of flame dynamics, backing fires and flanking fires both exhibit higher temperature residence times and backing fires exhibit a higher combustion factor. A redesigned experiment with a greater degree of replication may result in more conclusive results being achieved.

5. Conclusions

The properties of PyC produced by the application of three different FSMs to forest litter fuels burnt in a combustion wind tunnel have been investigated with ^{13}C NMR spectroscopy. Only one statistically significant result was found, which involved higher aryl carbon levels in ash from heading fires compared to flanking fires. PCA results shed light on the possibility that increasing the residence time of high temperature combustion as well as the combustion factor could be a potential method for increasing the production of aryl and O-aryl carbon from fire. Such actions may have positive benefits for the overall PyC balance through storing recalcitrant carbon in soils for extended periods of time.

6. Acknowledgements

The authors thank Janine McGowan for her assistance with the NMR experiments and data analysis. N. S thanks Michael Battaglia and Sandra Eady for their support of this project.

References

[1] Bowman, D. M. J. S. *et al. J. Biogeogr.* 38, (2011), 2223–2236.

[2] Moritz, M. A. *et al. Nature.* 515, (2014), 58–66 .

[3] Surawski, N. C. *et al*. *Nat. Commun*. 7, Article Number: 11536, (2016).

[4] Van der Werf, G. R. *et al*. *Earth Syst. Sci. Data.*, 9, (2017), 697-720.

[5] Le Quere, C. et al. *Earth Syst. Sci. Data.* 10, (2018), 405-448.

[6] Santín, C. et al. *Glob. Change Biol.* 22, (2016), 76-91.

[7] Santín, C. et al. 2015. *Glob. Change Biol.* 21, (2015), 1621-1633.

[8] Penman, T. D. et al. *Int. J. Wildland Fire.* 20, (2011), 721-733.

[9] Chandler, C. *et al*. 1983. Fire in Forestry 2: Forest Fire Management and Organization. John Wiley & Sons, New York.

[10] Tolhurst, K. G. and N. P. Cheney. Synopsis of the knowledge used in prescribed burning in Victoria. East Melbourne, Victoria: Department of Natural Resources and Environment (1999).

[11] National Wildfire Coordinating Group Fire Use Working Team. 2001. Smoke Management Guide for Prescribed and Wildland Fire, in*:* C. C. Hardy, R. D. Ottmar, J. L. Peterson J. E. Core, P. Seamon , (Eds.) (2001).

[12] Keene, W. C. *et al*. *J. Geophys. Res.-Atmos.* 111, Article Number: D04301, (2006).

[13] Surawski, N. C. *et al*. 2015. *Atmos. Chem. Phys.* 15, (2015), 5259-5273.

[14] Wehrens, R. 2011. *Chemometrics with R. Multivariate Data Analysis in the Natural Sciences and Life Sciences,* New York, USA, Springer.

[15] Husson, F. *et al*. 2018. FactoMineR: Multivariate Exploratory Data Analysis and Data Mining.

[16] Kassambara, A. and F. Mundt. 2017. factoextra: Extract and Visualize the Results of Multivariate Data Analyses.

[17] Zuur, A. *et al*. 2007. *Analysing Ecological Data,* New York, Springer.

[18] Sullivan, A. L. *Competitive Thermokinetics and Non-linear Bushfire Behaviour.* PhD thesis, Australian National University, Canberra, Australia, 20078

[19] Sullivan, A. L. and R. Ball. *Atmos. Environ.* 47, (2012), 133-141.

[20] Ball, R. *Clim. Res.* 59, (2014), 125-133.

[21] Ball, R. et al. *Combust. Theor. Model.* 8, (2004), 281-291.