

Investigation into the organic molecules present in leachate of soils affected by wildfire and fire retardant using ^{13}C NMR spectroscopy



Garrett Grubisa, Dr. Bruno Cinel (Supervisor), Dr. Sharon Brewer (Co-supervisor)

Thompson Rivers University, Department of Chemistry



Purpose

- Develop a sampling plan and experimental procedure to detect organic molecules present in an *in situ* laboratory leaching experiment of fire affected soils
- Add treatments of fire retardant to investigate changes to any molecules present

Background

- Wildfire activity within British Columbia and North America has substantially increased within recent years. The 2023 fire season in British Columbia officially surpassed the 2018 season as the most destructive ever recorded in terms of area burned.¹
- Although there has been some recent research into the effects of wildfires,^{2,3} there remains a need for further studies on the use of fire retardant and its impact on groundwater quality.
- Soils affected by intense wildfire activity have been shown to contain aromatic compounds with nitrogen substituents, benzene dicarboxylic acids, tricarboxylic acids, and tetracarboxylic isomers (BPCAs).²
- This research project involves using ^{13}C nuclear magnetic resonance (NMR) spectroscopy as an analytical tool to investigate the use of retardant on fire affected soils.

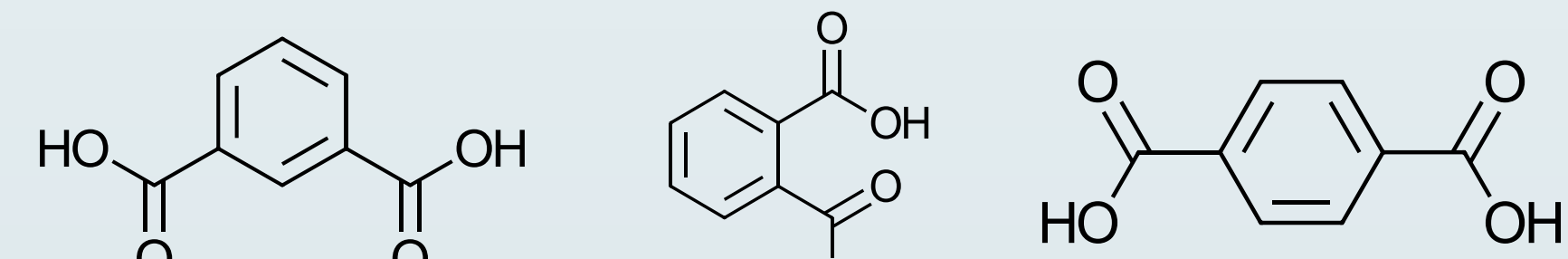


Figure 1. Three BPCAs identified in burnt soils³ (phthalic acids)

Experimental

Soil Sampling

- Fire affected soil samples were collected from the 2023 Bush Creek East wildfire around Adams Lake within the interior of British Columbia.



Figure 2. Sampling plot (0.3 m x 0.3 m) was excavated to 5cm deep.

Experimental

- Soil samples were dried at room temperature for 2 weeks
- Soil was sieved using a 2mm sieve to ensure homogeneity and remove large solids

Leaching Experiment

- 100.0 g of prepared soil was placed in 500 mL chromatography columns

Table 1. Leaching experiment solvent amounts and retardant additions.

Control Conditions	Experimental Conditions
100 mL water	100 mL water + 10 mL retardant
100 mL methanol	100 mL methanol + 10 mL retardant
100 mL ethyl acetate	100 mL ethyl acetate + 10 mL retardant



Figure 3. Leaching experiment of dry soil (left) and beginning of water + retardant.

- Leachate was collected after 24 hours into round bottom flasks and concentrated to dryness by rotary-evaporation
- Samples were sealed and stored below 0 °C until analysis
- Samples were analyzed by 1D ^{13}C NMR with proton decoupling using CDCl_3 or DMSO-d_6 as a solvent (25600 scans)

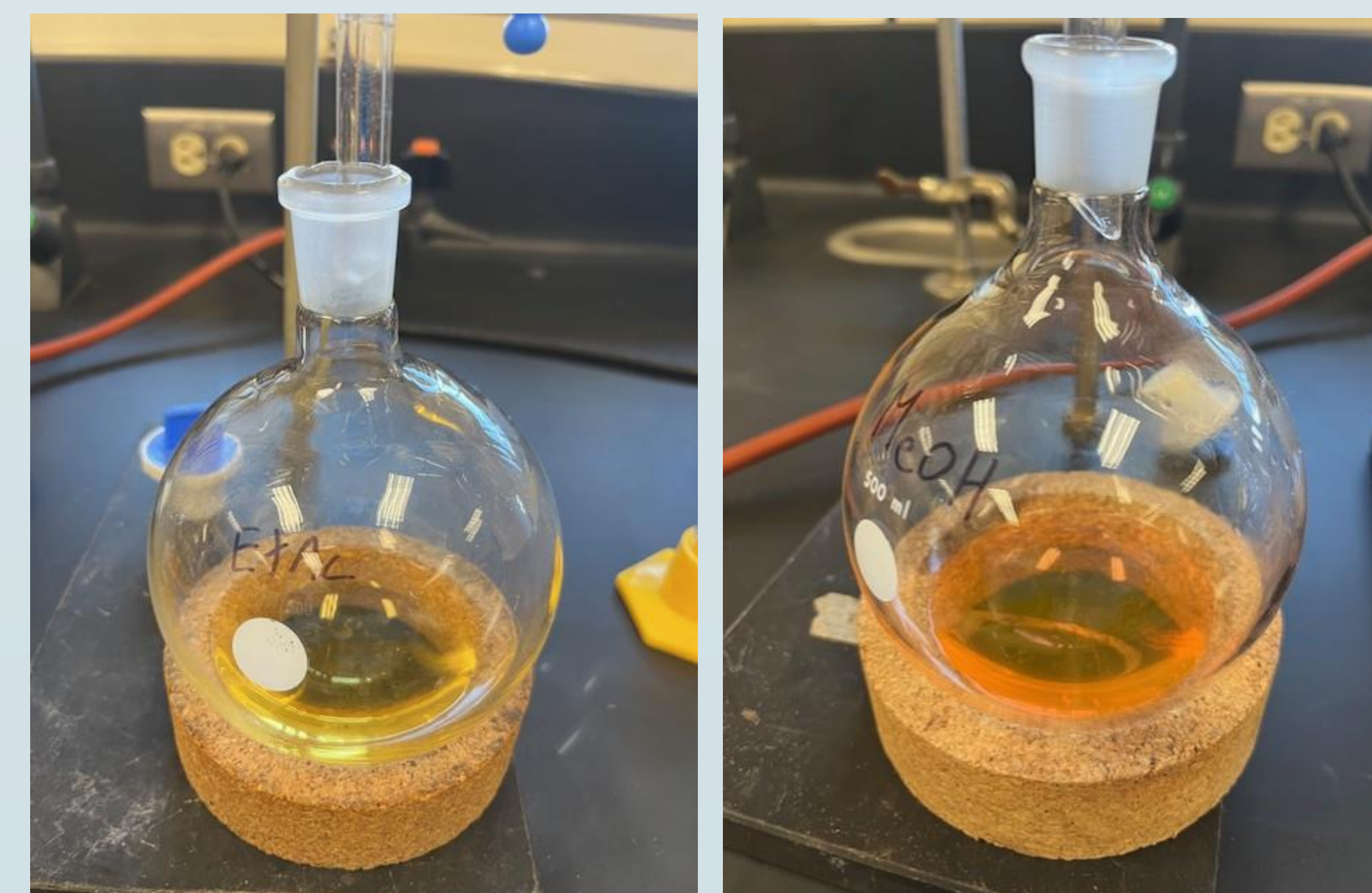


Figure 4. Leachate extracts for retardant + ethyl acetate (left) and retardant + methanol (right).

Results

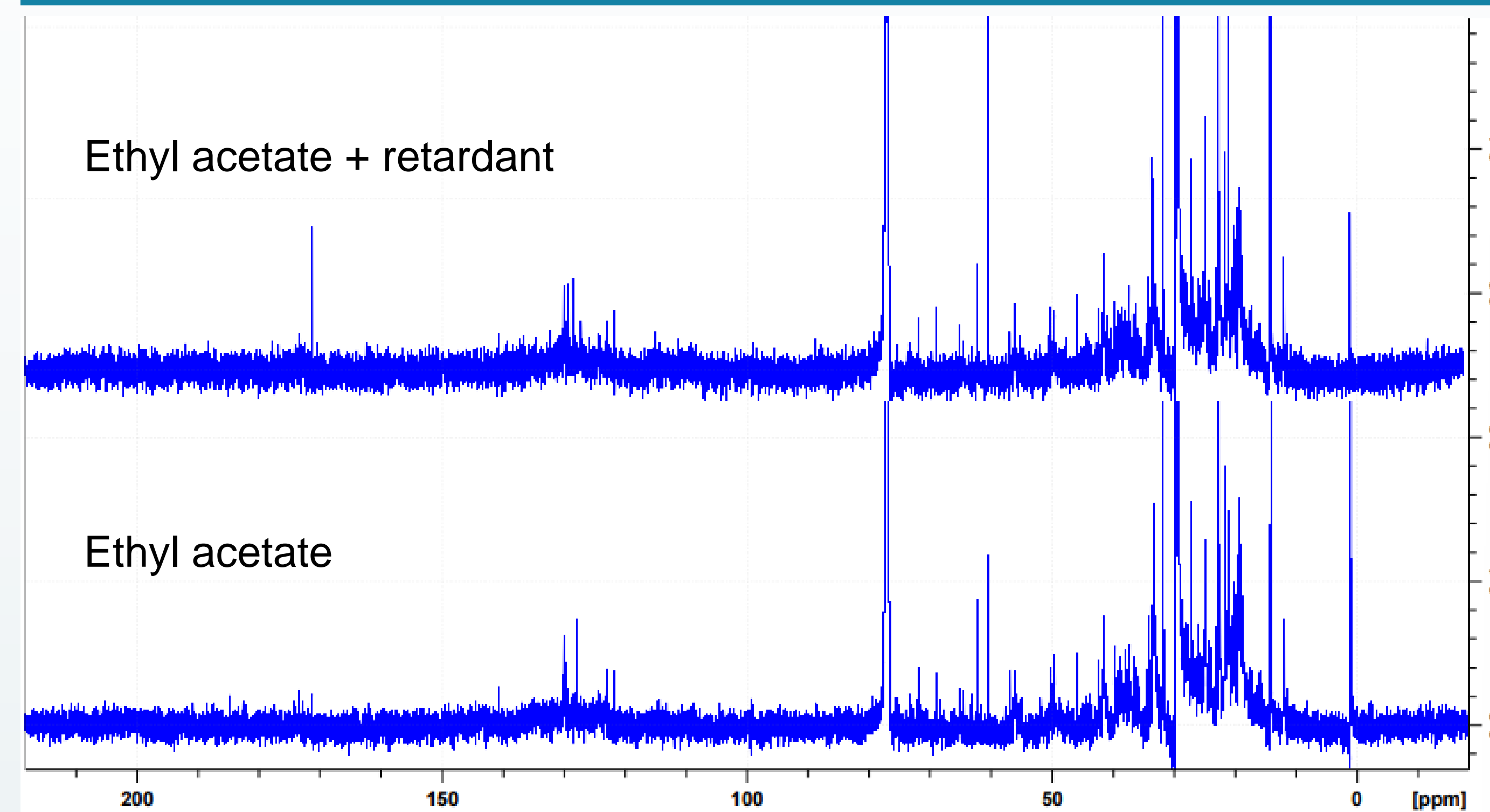


Figure 5. ^{13}C NMR spectra of ethyl acetate leachate (bottom) and ethyl acetate + retardant leachate (top).

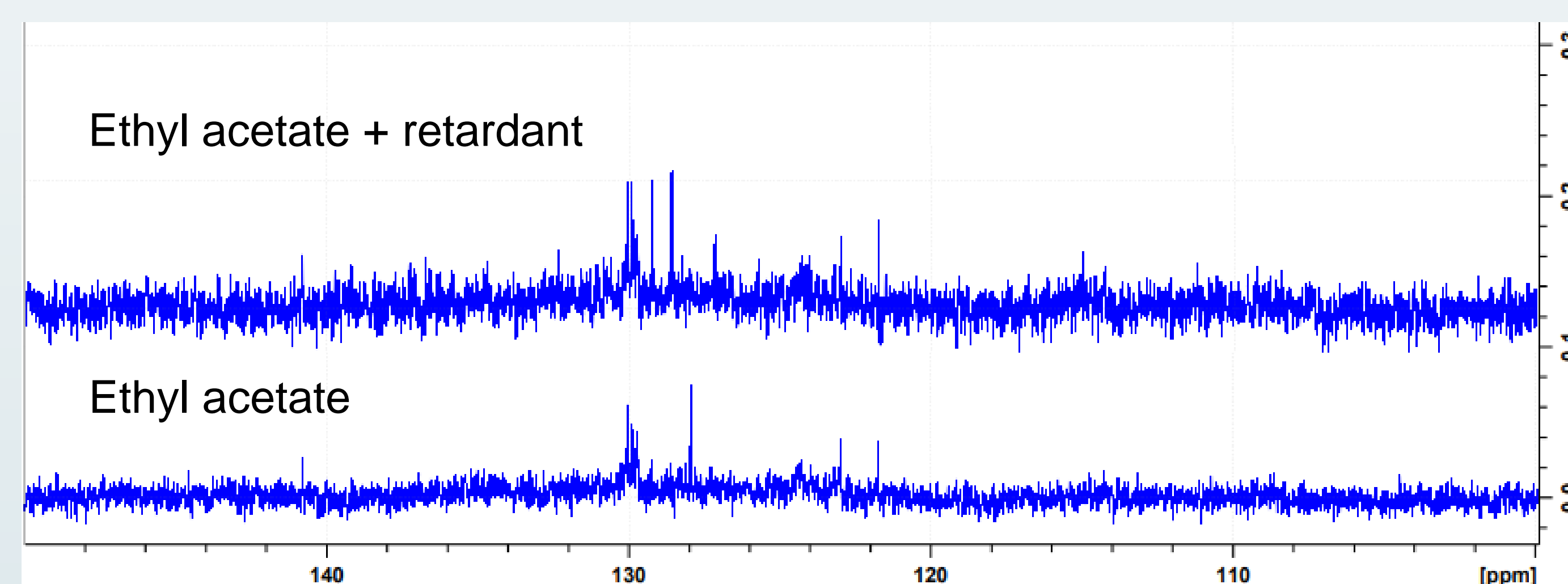


Figure 6. ^{13}C NMR spectra of ethyl acetate leachate (bottom) and ethyl acetate + retardant leachate (top) focused on aromatic region (100-150 ppm).

- The water solvent control and experimental column conditions did not contain many peaks in the spectra
- The methanol solvent control and experimental column conditions contained peaks similar to ethyl acetate solvent conditions
- Minimal changes in spectra in the 0-50 ppm region (CH_3 , CH_2 , CH signals) and the 50-100 ppm region (C-O signals)
- Appearance of a strong peak at ~170 ppm in the ethyl acetate + retardant conditions which is not present in the control ethyl acetate conditions
- Could indicate presence of BPCAs (COOH carbon signal)
- Ethyl acetate and methanol solvent conditions both displayed several peaks in the aromatic region (100-150 ppm) confirming presence of aromatics in burnt soils described in literature^{2,3}
- Indicates possible presence of BPCAs
- Greatest change in the ethyl acetate solvent conditions spectra involved the aromatic region (100-150 ppm)
- New strong peak present at ~129 ppm in ethyl acetate + retardant conditions
- New smaller peaks also present at 115, 127, and 132 ppm

Conclusion

- NMR can be an effective tool for detection of organic molecules present within leachate of fire affected soils
- There are chemical differences in the ^{13}C NMR spectra of fire affected soil leachate between samples treated with fire retardant and those untreated

Future Work

- Further develop leaching procedure to accommodate water solvent conditions
- Explore other analytical instruments for detecting organic molecules present in leachate of fire affected soils
- Expand the sampling procedure to allow for more samples from different fire affected areas
- Determine if fire retardant has the same impact on the organic molecules present in soils unaffected by fire

Acknowledgements

I would like to thank Dr. Bruno Cinel for his guidance, knowledge and commitment throughout this research project. I would also like to thank Dr. Sharon Brewer for her guidance and input as my co-supervisor. Additionally, the entire chemistry and NRS departments for their support in particular Dr. Jon Karakatsoulis, Thomas Pypker, and Darryl Carlyle-Moses.

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