Identification and Quantification of Gaseous Organic Compounds Emitted from Biomass Burning using Two-Dimensional Gas Chromatography/Time-of-Flight Mass Spectrometry

Hatch et al.

We thank the referees for their comments, which have helped to improve our manuscript. Our responses are provided below. The main text including 'track changes' is attached at the end of this file.

Referee #1

The authors present results from an experimental study exploring the identification and quantification of non-methane organic compounds (NMOCs) emitted from 6 fuels. In this study 722 compounds were either positively or tentatively identified and for the first time sesquiterpenes were identified in gas-phase BB emissions. The study and the manuscript are well organized and documented. Nevertheless I have several comments before this manuscript can be accepted for publication in Atmospheric Chemistry and Physics.

Questions: Page 23241, Line 24: How were the samples brought back to the lab? Were plants uprooted or just their leaves/pine needles used as samples? Can you describe potential differences in gas-phase products that one might expect between these two types of samples? How long were samples kept prior to experiments? I see that it is listed in section 3.35 but it needs to be listed in the experimental.

An overview of the fuels and their treatment during FLAME-4 has been provided by *Stockwell et al*. (2014). For coniferous fuels, fresh, green boughs (branches with needles attached) were cut and burned. For grasses/straw, stems were cut; they were not uprooted. Except ponderosa pine, which was cut locally, all fuel samples were shipped to the fire lab. Samples were stored for a few days to a few months prior to burning with the longer-term storage occurring in a humidified refrigerator. Storing cut plants likely reduces fuel moisture and possibly the emissions of biogenic compounds, as discussed in Section 3.5 for monoterpenes. *Stockwell et al*. (2014) also compared the FLAME-4 results to field measurements of fire emissions.

We have added the following text to section 2.1.1 (page 4, lines 15-18):

"The fuel treatment during FLAME-4 has been described by *Stockwell et al.* (2014). In general, fuel samples were shipped to the FSL and stored from a few days to a few months with longer-term storage occurring in a humidified refrigerator; instances identified where storage time may have influenced emissions are noted in Section 3.3."

Page 23243, Line 6: What percentage of semi-volatile compound loss is expected from the tubing? This can be tested by taking a semi-volatile compound and flowing through your system measuring the concentration before and after to determine loss. This should also be tested for SQT.

Loss of semi-volatile compounds during sampling is a well-known problem that requires systematic characterization, which is beyond the scope of this manuscript. All sampling methods have artifacts and we have done our best to minimize these in our sampling setup and analysis. In particular, Teflon tubing is often used for NMOC analysis; for example, minimal sampling artifacts (<10%) were observed for a standard mix of NMOCs following 200 m of Teflon tubing (*Schnitzhofer et al*., 2009), which is more than 20x longer than the tubing used in this study. As a specific example, sesquiterpenes are among the least volatile compounds detected in this work. *Helmig et al*. (2004) found ~90% recovery for sesquiterpenes after passing through nearly 4 m of PTFE tubing. Further, *Pollmann et al*. (2005) found nearly complete recovery of sesquiterpenes after passing through a sodium thiosulfate impregnated filter at low ozone concentrations. Therefore, we expect—for the compounds reported in this work—that losses to surfaces were minimal and within the reported the uncertainties. Although sampling losses likely influenced the range of compounds that could be detected.

In section 3.3.5, we have added the following text (Page 19, line 33):

"*Helmig et al*. (2004) found high (~90%) recoveries for sesquiterpenes following nearly 4 m of Teflon tubing."

Page 23243, Line 20: Typically glass-fiber filters are baked at ~ 600 C to remove adventitious carbon. How do you know that these filters have been baked at a high enough sample to remove impurities?

We recognize that filters are typically baked at much higher temperatures and acknowledge that baking at ~130 C likely did not completely remove all impurities, particularly those with lower volatility. The room temperature desorption method used to extract the analytes targets much higher volatility compounds than the solvent extraction methods that are often used with filter samples. Therefore, pre-baking to 600 C was not necessary in this case. Further, the compounds presented in Table 2 were not observed in the blank and background filters that were treated in the same manner. Thus, although other impurities may be present, it does not negate that the reported compounds can be attributed to biomass burning smoke.

Page 23244, Line 1: What were the typical masses of the background and after PM collection?

The PM collected on the background filter was negligible, compared to a net gain of up to ~3 mg for the smoke samples.

Page 23247, Line 20: What oxygenated compounds displayed high breakthrough? These should be asterisked in tables and charts.

As indicated in the caption of Table A1, all compounds that we believe may be underestimated are listed in italics. We have now mentioned this in the text, as well, towards the end of section 3.1 (page 10, line 4).

Page 23251, Line 20: Need to direct reader to Table A1 for abundance of benzene and toluene. How much are your measurements under predicting these values? Why are you under predicting?

We have added a reference to Table A1. The underestimation of benzene/toluene (due to MS detector saturation) is discussed in section 2.3; we have added a reference to this section (page 13, line 9). A comprehensive comparison of FLAME-4 NMOC measurements using four different techniques will be presented in a separate study.

Page 23257, Line 24: Why could the relative mass of needle vs. wood not be determined? What are you visually observing?

The relative mass could not be determined because the branches were burned intact and not as separated piles of twigs and needles. There is no way to measure the pre-fire mass of the needles and wood separately without destroying the natural fuel geometry. Thus it is difficult to reasonably estimate the relative masses of needles and twigs. However, after the fires most of the needles were gone, but much of the wood was only charred.

Page 23260, Line 1: Is there information regarding the lignin content of the plant fuels used in this study?

We assume the referee is referring to page 23261, lines 1-2 where we discuss potential differences in lignin content between the two grass species measured in this study. Unfortunately, we could not find published literature stating the lignin content of these grasses, nor was it measured in this study. We stated as such on page 23261, line 3. To clear up the confusion we have revised the sentence to "Although the biomass composition of these grasses have not been **reported.**"

Minor Questions: Page 23241, Line 16: What differences can potentially occur if the fuel sample is not standing upright?

The fuel arrangement can influence the combustion conditions. Piles of grasses will likely burn under relatively more smoldering conditions than grasses standing upright.

Page 23246, Line 25: What vapor pressure ranges are not characterized by this approach?

In Section 3.1, we have added the vapor pressures for the compounds roughly bounding this GCxGC measurement range (3-methyl 1-butene and sesquiterpenes) (Page 9, lines 3 & 20).

Page 23247, Line 1: What is the polarity range that can be used for GC?

The accessible polarity range depends on the sampling method and GC columns used for analysis, as well as the thermal stability of the analyte compounds. Further, molecular polarity is not a well-defined property (*Pankow and Barsanti*, 2009), and thus it is not straightforward to define the measureable polarity range. As a full description of GC methods is outside the scope of this manuscript, we provided examples of compounds that did not elute under the GCxGC conditions of this study (page 23247, lines 2-3).

Page 23254, Line 2: How much higher are 1-alkenes relative to C12. How much higher are terminal alkene SOA yields relative to internal alkenes?

For the first question, we assume the referee is asking how much higher the SOA yields are for 1-alkenes relative to alkanes (up to C12). Per the data presented in *Ziemann* (2011), there is not a consistent difference in the SOA yields between the 1-alkenes and linear alkanes, with the alkene SOA yields ranging from ~17-117% higher. Similarly, SOA yields for the terminal alkenes range from ~20-380% higher than internal alkenes. We have added these estimates to the text (page 16, lines 1-3).

Page 23259, Line 6: How much error do you expect?

We have updated the text to (page 19, lines 16-19): **"Considering the wide range of reported SOA yields among the MT isomers (<10-60% (*Griffin et al.*, 1999; *Lee et al.*, 2006)),** prediction errors may be significant considering the large contribution of these species in the smoke of coniferous fuels (Figures 1 and 2)."

Page 23259, Line 16: What are their volatilities and atmospheric lifetimes?

We have revised the sentence to (page 19, lines 28-32):

"SQTs have historically been difficult to measure (*Bouvier-Brown et al*., 2009; *Pollmann et al*., 2005) due to their relatively low volatilities **(P_{vap}, ~1×10^{-3} kPa at 25 °C (*Helmig et al.*, 2003)**) and high reactivities **(atmospheric lifetimes on the order of minutes to hours** (*Atkinson and Arey*, 2003))."

Page 23259, Line 22: What are negligible ozone concentrations?

We have changed 'negligible' to '**near-zero**'.

Page 23261, Line 6: What were the levoglucosan concentrations in WG compared to the other fuels?

Because only the fraction of the levoglucosan marker (via AMS measurements) was reported in the cited study, as opposed to levoglucosan concentrations, we have decided to eliminate this comparison.

Page 23262, Line 14: This sentence should be more quantitative.

We have updated the sentence to (page 22, lines 9-11):

"However, due to the small molecular sizes **(<C_7)** and relatively low concentrations of the observed compounds **(~2-11% of the total EF),** they are not likely to contribute significantly to BB SOA."

Table 3: The estimated SOA mass could be better constrained by using average OH, O3,

and NO3 atmospheric steady state concentrations, typical gas-phase bimolecular rate constants for the category of interest and SOA mass yields. Assuming that each compound reacts completely is not a fair estimate of SOA mass since some compounds react very slow.

We have updated Table 3 with SOA estimates that account for differences in OH-reactivity among the compound classes.

Figures 1-6: Having the GC spectra is not necessary in each figure and should be put in supplemental information. Axis and labels are very small they font should be increased.

The authors collectively and respectfully disagree that the GCxGC chromatograms are not necessary. We think that they provide a strong visual representation of the complexity of biomass burning NMOC emissions. Further, as this is the first reported application of GCxGC for the analysis of gas-phase BB emissions and 2D-chromatograms are not widespread in the related literature, we think it is important to retain the chromatograms in the manuscript.

We have adjusted the colorscale to better highlight the minor peaks. The font size has also been increased.

Minor Comments: Several sentence need references, some examples below: Page 23238: Line 23, and Line 25; Page 23239: Line 3; Page 23252: Line 26; Page 23255, Line 1; Page 23261, Line 1.

We have added references where needed.

Page 23238, Line 24: Sentence is awkward, revise.

We have revised the sentence to "Wildfires and prescribed burns occur globally with highly variable fuel types and burning conditions."

Page 23251, Line 23: Sentence is awkward, revise.

The sentence has been revised to: "Further, higher molecular weight aromatic HCs were detected than are typically reported elsewhere (e.g. ≤C_9, (*Akagi et al*., 2011; *Andreae and Merlet*, 2001); more recently, unspeciated C_{11} alkyl aromatics (*Yokelson et al*., 2013)).

Page 23251, Line 25: Compilations is an odd word to use here.

We have changed to 'BB reviews'.

Page 23251, Line 3: Extra period after fuels

The error has been corrected.

Page 23253, Line 2: Awkward sentence, revise.

We have revised the sentence to:

"Guaiacols are commonly measured in smoke from coniferous fuels (*Jiang et al*., 2010; *Saiz-Jimenez and De Leeuw*, 1986), as these softwoods contain lignins composed primarily of guaiacyl units (*Shafizadeh*, 1982)."

Page 23253, Line 11: There is an additional reference from this group that also shows aqueous-phase reactions with OH and phenols have 100% SOA mass yields.(Sun et al., 2010)

We have included the suggested reference.

References Sun, Y.L., Zhang, Q., Anastasio, C., Sun, J., 2010. Insights into secondary organic aerosol formed via aqueous-phase reactions of phenolic compounds based on high resolution mass spectrometry. Atmos. Chem. Phys. 10, 4809-4822.

Referee #2:
This paper presents results of highly detailed analyses of sorbent tube samples collected during laboratory test burns of 6 biomass fuels during the FLAME-IV study. Thermal-Desorption 2D-GC-TOF-MS analysis was conducted on gaseous non- methane organic compounds (NMOC; ranging from 'volatile' to 'intermediate volatility') extracted from Tenax/Carbon sorbent tubes collected from well mixed smoke collected during the FLAME studies. A large number of compounds were identified and quantified based on instrument response to either authentic standards of identified com- pounds or chemically similar compounds. The analysis described in the paper appears to be carefully done, with sources of uncertainty identified and the results placed in context with prior investigation in this area. The data and analysis will be of great interest to a wide swath of researchers investigating atmospheric impacts of biomass burning (BB) emissions. These results and discussion will be of particular interest atmospheric modelers and those studying the potential precursors for the secondary organic aerosol (SOA) production observed in biomass burning emissions (which are, as noted, substantially under-predicted by current models and a large source of uncertainty in models). Therefore, the paper is highly suitable for publication in ACP. I concur with most of the questions raised by the other referee, so look forward to these points being addressed. Here I highlight some (mostly) minor points, mostly with the aim of improving the clarity of the manuscript.

P23239, L8-9: This example is not the best way to demonstrate the health and environmental impacts of long range transport of BB emissions – not so many folks in the Arctic.

We have included a different example showing the influence of Siberian wildfires on ozone concentrations in North America (page 2, lines 16-17).

P23243, L7-8: Considering the extensive testing conducted to look at sorbent breakthrough and volatilization from the filters, it is surprising that so little attention is paid here. Some effort to quantify the extent of this effect and identify compounds that might be under-estimated because of this potential source of compound loss would be very helpful.

Sesquiterpenes are among the least volatile compounds detected in this work. *Pollmann et al*. (2005) found nearly complete recovery of sesquiterpenes after passing through a sodium thiosulfate impregnated filter at low ozone concentrations. Further, *Helmig et al*. (2004) found ~90% recovery for sesquiterpenes after passing through PTFE tubing. Therefore, we expect—for the compounds reported in this work—that losses to surfaces were minimal and within the reported the uncertainties. Although sampling losses likely influenced the range of compounds that could be detected.

In section 3.3.5, we have added the following text (Page 19, line 33):

"*Helmig et al*. (2004) found high (~90%) recoveries for sesquiterpenes following nearly 4m of Teflon tubing."

P23244, L1-2: This sentence doesn't make sense to me. How would you know if mass was loss from the background filter during PM collection? Perhaps 'PM collection' should be 'filter desorption'? In any case, this description should be clarified.

To avoid confusion, we eliminated this problematic statement. The PM collected on the background filter was negligible, compared to a net gain of up to ~3 mg for the smoke samples.

P23245, L10: GC Column types are not listed, though are referred to later. It would be helpful to list them here.

We have added the GC column types to the text (page 7, lines 18-21).

P23245, L21-22: I found this description of background correction in general unclear. What statistical method was applied to test whether peaks were 'statistically different from zero'?

We have made minor changes to the text to improve the clarity and modified 'statistically different from zero' to (Page 7, lines 31-32):

"Compounds were removed from consideration if their concentrations were **negative or not significantly different from zero following background subtraction**."

P23246, L1-7: How was the most chemically similar compound determined? Are there cases where this selection would have a large effect on the quantification of the compound, and if so is this accounted-for in the uncertainty calculation? Also, I found the distinction between the use of the calibration line and the response factor unclear.

We have modified the text to clarify the distinction between calibration curves and response factors. Regarding determination of the most chemically similar standard, we have added the following text (Page 8, lines 6-11):

"Tentatively identified analytes were quantified using the calibration curve of the most chemically similar standard compound, **as determined by comparing functional groups, carbon number, degree of unsaturation/conjugation, and aromaticity. Given the large number (~275) and wide range (Table A1) of standard compounds analyzed in this work, reasonable surrogate standard compounds were available for most of the compounds detected in the biomass burning samples**."

Differences in instrument sensitivity between the analytes and surrogate standards may have an influence on the quantification; therefore we have adjusted the minimum uncertainty to 50% of the reported EFs for these compounds (compared to 20% minimum for compounds with associated standard compounds).

P23246, L25: What is meant by 'lower volatility compounds' and 'not well characterized'? Some attempt at quantifying the range of volatility identified (e.g. vapor pressures, RT, C*), and the uncertainty in quantification should be included (also relates to discussion of sampling losses above).

We have eliminated the questionable sentence. In Section 3.1, we have added the vapor pressures for the compounds roughly bounding the GCxGC measurement range (3-methyl 1-butene and sesquiterpenes).

P23247, L4-7: What effect does this 'wrap around' have on the quantification of these and neighboring compounds? Can this be specified and is it reflected in uncertainties for these compounds?

Wrap around should not significantly affect the quantifications of neighboring compounds due to the high sampling rate of the time-of-flight mass spectrometer and mass spectral deconvolution capabilities of the analysis software. The quantification of compounds that wrapped around and have an associated standard (e.g., furfural, phenol) should also not be significantly impacted because the calibration curves were generated under the same instrument conditions (i.e., wraparound was the same). However, the wraparound effect may influence quantifications that were performed using surrogate standards. A compound that wrapped around but quantified with a standard that did not is likely underestimated and vice versa. We note that the minimum error bars were increased to 50% of the reported EF for the tentatively identified compounds to account for the possible differences in instrument sensitivity between the analytes and surrogate standards.

We have added the following text in section 3.1 (page 9, lines 13-18):

"Such wraparound effects should not influence the quantification of the positively identified compounds because these effects were captured in the calibration curves. For a limited number of compounds, wraparound may have influenced quantifications of tentatively identified compounds that wrapped around and were quantified with a surrogate standard compound that did not (or vice versa)."

P23247, L24-27: Given that values with which to compare are available, this comparison should be made and the extent by which these values are 'lower bounds' reflected in the discussion and the table.

A full comparison of all NMOC measurements by four different techniques during FLAME-4 is underway and will be presented elsewhere. We have added a statement to that effect in the text (page 10, lines 8-9). Values that we believe are underestimated are listed in italics in Table A1.

P23249, L23: Presumably 'compounds emitted during smoldering combustion'?

We have implemented the suggested wording.

P23250, L14: This would suggest that it cannot be at all explained by differences in MCE?

We have eliminated the word 'entirely'.

P23255, L27: Disproportionately relative to what?

We have eliminated the word 'disproportionately'.

P23256, L6-9: It is not clear why NO2/NO ratio is discussed here and whether high- or low-NOx yields should be applied? Should this be VOC/NOx?

The text correctly references NO2/NO ratios. As described in *Chan et al*. (2010), the SOA formation from unsaturated aldehydes through a PAN channel is dictated by the ratio of NO2/NO. Given the significant emissions of unsaturated aldehydes from biomass burning and the relatively high NO2/NO ratios in smoke plumes, we are postulating that such pathways occur in smoke plumes and may have a significant influence on the SOA yields from these light aldehydes. We refer the reader to the Chan et al (2010) reference for further information.

P23256, L23: 'Largest category' is ambiguous. Referring to the figure I presume it is largest mass emission factor, but this could be interpreted to mean the largest number of identified compounds. This kind of ambiguity is found in several other places and I suggest that the revised manuscript be edited with an eye towards removing such ambiguity.

The text stated "the largest category in BS smoke by EF". We have revised it to "the largest EF category in BS smoke…" and clarified other ambiguous references throughout the text.

P23257, L25: 'Visual observations' of the mass of fuel burned? This seems fairly untrustworthy? Can this be quantified in any way?

Unfortunately, this cannot be quantified any more reliably than indicated. There is no way to measure the pre-fire mass of the needles and wood separately without destroying the natural fuel geometry. However, after the fires most of the needles were gone, but much of the wood was only charred.

P23258, L14: No correlations are presented here.

We have changed ‘correlations’ to ‘similarities’.

P23259, L5-11: This is the first mention of PTRMS data in the manuscript, and there’s little reasoning behind this sudden comparison (nor is the acronym defined) or references to works that rely on these values, and what the issues with that might be. Some context should be provided. Further, while the suggestions in this paragraph are likely quite welcome, it would help if a bit further guidance is provided. For example, if ratios from essential oil samples are used, how might these be normalized for use in as emission factors for modeling purposes? This discussion might be transferred to the conclusions section.

We have eliminated the PTRMS comparison at this point in the manuscript. If unspeciated measurements of MTs are available, this could be distributed over the relative proportions of specific isomers reported for steam-distilled essential oils. We have added this suggestion to the text.

P23260, L28: Should be section 3.3.2

We thank the referee for catching this mistake. It has been corrected.

P23265, L8-10: The references listed include OA enhancement ratios for some of these same fuels under similar conditions. Why not do a direct comparison, where possible?

The primary goal of the SOA calculations was to demonstrate the relative importance of the major chemical classes and not necessarily to reproduce measured OA enhancements. These cited references typically report OA enhancement ratios for a single burn per fuel. Given the high variability of emissions from burn to burn and oxidation conditions among smog chamber experiments, direct comparisons to past experiments is difficult. Further, we do not expect that we are capturing all of the compounds contributing to SOA formation, nor the dynamics of the system (e.g., POA evaporation). Thus we prefer to place our estimates in the context of the range of reported OA enhancements.

Figures 1-6: The chromatograms don’t add much to the presentation, so can be moved to the supplement and the additional real-estate potentially used to selectively point out some noteworthy features of the bar charts.

The authors collectively and respectfully disagree that the GCxGC chromatograms are not necessary. We think that they provide a strong visual representation of the complexity of biomass burning NMOC emissions. Further, as this is the first reported application of GCxGC for the analysis of gas-phase BB emissions and 2D-chromatograms are not widespread in the related literature, we think it is important to retain the chromatograms in the manuscript.

References:

Akagi, S. K., R. J. Yokelson, C. Wiedinmyer, M. J. Alvarado, J. S. Reid, T. Karl, J. D. Crounse, and P. O. Wennberg (2011), Emission factors for open and domestic biomass burning for use in atmospheric models, Atmos. Chem. Phys., 11(9), 4039-4072.

Andreae, M. O., and P. Merlet (2001), Emission of trace gases and aerosols from biomass burning, Global Biogeochem Cy, 15(4), 955-966.

Atkinson, R., and J. Arey (2003), Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, Atmos. Environ., 37, S197-S219.

Bouvier-Brown, N. C., A. H. Goldstein, J. B. Gilman, W. C. Kuster, and J. A. de Gouw (2009), In-situ ambient quantification of monoterpenes, sesquiterpenes, and related oxygenated compounds during BEARPEX 2007: implications for gas- and particle-phase chemistry, Atmos. Chem. Phys., 9(15), 5505-5518.

Chan, A. W. H., M. N. Chan, J. D. Surratt, P. S. Chhabra, C. L. Loza, J. D. Crounse, L. D. Yee, R. C. Flagan, P. O. Wennberg, and J. H. Seinfeld (2010), Role of aldehyde chemistry and NOx concentrations in secondary organic aerosol formation, Atmos. Chem. Phys., 10(15), 7169-7188.

Griffin, R. J., D. R. Cocker, R. C. Flagan, and J. H. Seinfeld (1999), Organic aerosol formation from the oxidation of biogenic hydrocarbons, J. Geophys. Res., 104, 3555-3567.

Helmig, D., F. Bocquet, J. Pollmann, and T. Revermann (2004), Analytical techniques for sesquiterpene emission rate studies in vegetation enclosure experiments, Atmos. Environ., 38(4), 557-572.

Helmig, D., T. Revermann, J. Pollmann, O. Kaltschmidt, A. J. Hernandez, F. Bocquet, and D. David (2003), Calibration system and analytical considerations for quantitative sesquiterpene measurements in air, J Chromatogr A, 1002(1-2), 193-211.

Jiang, G. Z., D. J. Nowakowski, and A. V. Bridgwater (2010), Effect of the Temperature on the Composition of Lignin Pyrolysis Products, Energy Fuels, 24, 4470-4475.

Lee, A., A. H. Goldstein, J. H. Kroll, N. L. Ng, V. Varutbangkul, R. C. Flagan, and J. H. Seinfeld (2006), Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, J. Geophys. Res., 111(D17).

Pankow, J. F., and K. C. Barsanti (2009), The carbon number-polarity grid: A means to manage the complexity of the mix of organic compounds when modeling atmospheric organic particulate matter, Atmos. Environ., 43(17), 2829-2835.

Pollmann, J., J. Ortega, and D. Helmig (2005), Analysis of atmospheric sesquiterpenes: Sampling losses and mitigation of ozone interferences, Environ. Sci. Technol., 39(24), 9620-9629.

Saiz-Jimenez, C., and J. W. De Leeuw (1986), Lignin pyrolysis products: Their structures and their significance as biomarkers Organic Geochemistry, 10(4-6), 869-876.

Schnitzhofer, R., A. Wisthaler, and A. Hansel (2009), Real-time profiling of organic trace gases in the planetary boundary layer by PTR-MS using a tethered balloon, Atmos. Meas. Tech., 2(2), 773-777.

Shafizadeh, F. (1982), Introduction to Pyrolysis of Biomass, J Anal Appl Pyrol, 3(4), 283-305.

Stockwell, C. E., R. J. Yokelson, S. M. Kreidenweis, A. L. Robinson, P. J. DeMott, R. C. Sullivan, J. Reardon, K. C. Ryan, D. W. T. Griffith, and L. Stevens (2014), Trace gas emissions from combustion of peat, crop residue, biofuels, grasses, and other fuels: configuration and FTIR component of the fourth Fire Lab at Missoula Experiment (FLAME-4), Atmos. Chem. Phys., 14, 9727-9754.

Yokelson, R. J., I. R. Burling, J. B. Gilman, C. Warneke, C. E. Stockwell, J. de Gouw, S. K. Akagi, S. P. Urbanski, P. Veres, J. M. Roberts, W. C. Kuster, J. Reardon, D. W. T. Griffith, T. J. Johnson, S. Hosseini, J. W. Miller, D. R. Cocker, H. Jung, and D. R. Weise (2013), Coupling field and laboratory measurements to estimate the emission factors of identified and unidentified trace gases for prescribed fires, Atmos. Chem. Phys., 13(1), 89-116.

Ziemann, P. J. (2011), Effects of molecular structure on the chemistry of aerosol formation from the OH-radical-initiated oxidation of alkanes and alkenes, Int Rev Phys Chem, 30(2), 161-195.

Identification and Quantification of Gaseous Organic Compounds Emitted from Biomass Burning using Two-Dimensional Gas Chromatography/Time-of-Flight Mass Spectrometry

L.E. Hatch[1], W. Luo[1], J.F. Pankow[1], R.J. Yokelson[2], C.E. Stockwell[2], and K.C. Barsanti[1]

[1]{Department of Civil and Environmental Engineering, Portland State University, Portland, Oregon}

[2]{Department of Chemistry, University of Montana, Missoula, Montana}

Correspondence to: K.C. Barsanti (barsanti@pdx.edu)

Abstract

The current understanding of secondary organic aerosol (SOA) formation within biomass burning (BB) plumes is limited by the incomplete identification and quantification of the non-methane organic compounds (NMOCs) emitted from such fires. Gaseous organic compounds were collected on sorbent cartridges during laboratory burns as part of the fourth Fire Lab at Missoula Experiment (FLAME-4~~), with analysis~~) and analyzed by two-dimensional gas chromatography/time-of-flight mass spectrometry (GC×GC/TOFMS). The sensitivity and resolving power of GC×GC/TOFMS allowed the acquisition of the most extensive data set of BB NMOCs to date, with measurements for ~~722~~708 positively or tentatively identified compounds. Estimated emission factors (EFs) are presented for these compounds for burns of six different vegetative fuels, including conifer branches, grasses, agricultural residue, and peat. The number of compounds ~~detected from individual burns~~meeting the peak selection criteria ranged from 129 to 474 among individual burns, and included extensive isomer groups. For example, 38 monoterpene isomers were observed in the emissions from coniferous fuels; the isomeric ratios were found to be consistent with those reported in relevant essential oils, suggesting that the composition of such oils may be very useful when predicting fuel-dependent terpene emissions. Further, eleven sesquiterpenes were detected and tentatively identified, providing the first reported speciation of sesquiterpenes in gas-

phase BB emissions. The calculated EFs for all measured compounds are compared and discussed in the context of potential SOA formation.

1 Introduction

Biomass burning (BB) emissions can strongly influence tropospheric chemistry and climate~~.~~ (Crutzen and Andreae, 1990). Wildfires and prescribed burns occur ~~under conditions and~~globally with ~~biomass~~highly variable fuel types ~~that vary greatly.~~and burning conditions (van der Werf et al., 2010). Fires ~~emit~~lead to high concentrations of particulate matter (PM) and gases; such gases include nitrogen oxides (NO_x), carbon dioxide/monoxide, and non-methane organic compounds (NMOCs) of varying volatilities~~.~~ (Andreae and Merlet, 2001; Yokelson et al., 2013). During plume evolution, these emissions may react photochemically to form secondary pollutants (e.g., ~~ozone) (Crutzen and Andreae, 1990).~~ozone) (Goode et al., 2000; Hobbs et al., 2003). The primary emissions and secondary species affect human health and climate. Atmospheric PM is associated with negative health effects, such as cardiovascular and respiratory diseases ~~(Poschl, 2005)~~(Pope and Dockery, 2006). ~~Further, long~~Long-range transport of BB emissions can carry species 1000+ km from a fire source ~~(Crutzen and Andreae, 1990)~~(Crutzen and Andreae, 1990), thereby extending the health and environmental consequences of smoke well beyond fire-prone regions; for example, ~~emissions from wildfires occurring~~transport of Siberian wildfire emissions has contributed to non-attainment of ozone air quality standards in ~~Russia have impacted the Arctic~~ North America ~~(Wang et al., 2011)~~(Jaffe et al., 2004).

BB particles can influence the radiative balance of the atmosphere directly by scattering or absorbing solar radiation ~~(Hobbs et al., 1997)~~(Hobbs et al., 1997), and indirectly by acting as cloud condensation nuclei (CCN) ~~(Desalmand and Serpolay, 1985; Reid et al., 2005)~~(Desalmand and Serpolay, 1985; Reid et al., 2005) and ice nuclei (IN) ~~(Petters et al., 2009)~~(Petters et al., 2009). A large number of BB particles in a forming cloud can increase the number of CCN, yielding smaller cloud droplets, thereby increasing cloud albedo ~~(Crutzen and Andreae, 1990)~~(Crutzen and Andreae, 1990). This effect may alter precipitation patterns and thus the hydrological cycle (~~Lohmann and Feichter, 2005~~Lohmann and Feichter, 2005; Andreae et al., 2004).

BB is the second largest global source of NMOCs; ~~these~~emitted species may undergo photochemical processing (“aging”), leading to lower volatility or more soluble compounds that can condense into existing particles and form secondary organic aerosol (SOA) ~~(Kroll~~

~~and Seinfeld, 2008; Hallquist et al., 2009)~~(Kroll and Seinfeld, 2008; Hallquist et al., 2009). Laboratory and field studies have shown a wide range of organic aerosol (OA) mass enhancement ratios (<1 to 4) following aging of BB smoke ~~(Grieshop et al., 2009; Hennigan et al., 2011; Ortega et al., 2013; Jolleys et al., 2012; Yokelson et al., 2009;~~ (Grieshop et al., 2009; Hennigan et al., 2011; Ortega et al., 2013; Jolleys et al., 2012; Yokelson et al., 2009; Akagi et al., 2012~~; Wigder et al., 2013; Vakkari et al., 2014)~~; Wigder et al., 2013; Vakkari et al., 2014), demonstrating high variability in BB emissions and/or plume chemistry. ~~Further, Hennigan et al. (2011)~~Further, Hennigan et al. (2011) reported extensive oxidation of BB primary OA (POA) during laboratory aging experiments, suggesting that physicochemical properties of OA may change regardless of net loss or production of OA mass. Highly oxidized SOA and aged POA components can influence particle hygroscopicity ~~(Saxena et al., 1995)~~(Saxena et al., 1995) and CCN activity, thereby exacerbating the effects of BB-derived particles on biogeochemical cycles and planetary albedo.

Efforts toward understanding SOA formation in BB plumes have been hindered by limited identification and quantification of the NMOCs emitted by fires (Akagi et al., 2011). In a recent study using data from open-path Fourier transform infrared spectroscopy, proton-transfer-reaction ion-trap mass spectrometry, and gas chromatography/mass spectrometry (GC/MS), only ~50-70% of measured gas-phase organic mass was identified (Warneke et al., 2011; Yokelson et al., 2013), with the majority of the remaining mass likely having lower volatility than the NMOCs routinely measured in BB studies. Thus there is a ~~significant~~ need to better characterize NMOCs in BB smoke. Further, studies have demonstrated that known SOA precursors alone cannot explain observed OA growth in aged BB smoke (Grieshop et al., 2009; Ortega et al., 2013). Given the potentially significant production of SOA from BB, improved measurements of gas-phase SOA precursors within smoke plumes are essential for ~~better assessing~~understanding the health and climate impacts of BB particles.

Whereas traditional one-dimensional (1-D) GC/MS has been extensively applied toward the characterization of BB emissions ~~(Christian et al., 2004; Simpson et al., 2011; Ciccioli et al., 2001)~~(Christian et al., 2004; Simpson et al., 2011; Ciccioli et al., 2001), GC×GC has seen limited application in this field ~~(Ma et al., 2010; Ma and Hays, 2008; Nara et al., 2006)~~(Ma et al., 2010; Ma and Hays, 2008; Nara et al., 2006). GC×GC employs two columns to extend the separation capabilities allowed by 1-D GC. Typically, a non-polar column is utilized for the primary separation based on volatility; slices of the analyte flow are directed to a second column for separation according to polarity or polarizability (Beens et al., 1998). Several characteristics ~~(Mondello et al., 2008)~~(Mondello et al., 2008) of GC×GC/TOFMS make it a powerful tool for characterizing the highly complex gas-phase components of smoke. These are: (1) high resolving power provides enhanced chromatographic separation; (2) thermal modulation at the interface of the primary and secondary columns refocuses eluting peaks leading to significant improvements in signal-to-noise ratio and thus sensitivity; (3) high TOFMS spectral collection rate allows up to 500 full mass spectra (*m/z* 34-500) to be obtained for a given peak eluting from the secondary column (the time evolution of the mass spectra can help deconvolute co-eluting compounds); and (4) distinct compound classes form patterns in the 2-D retention space aiding in compound classification. Herein, the first application of GC×GC to broadly characterize the gas-phase emissions of BB is described, including comparisons among the emissions from burns of selected conifer, grass, crop residue, and peat fuel types.

2 Experimental

2.1 FLAME-4 Sampling

Samples were collected during the fourth Fire Lab at Missoula Experiment (FLAME-4) from November 3-12, 2012 in Missoula, Montana. ~~An overview of FLAME-4 has been provided by Stockwell et al. (2014)~~An overview of FLAME-4 has been provided by Stockwell et al. (2014). Controlled burns were conducted in the combustion laboratory of the US Forest Service Fire Science Laboratory (FSL) using a variety of vegetative fuels. The combustion laboratory is described in detail elsewhere ~~(Christian et al., 2004)~~(Christian et al., 2004). In these "room burn" experiments, smoke was allowed to mix throughout the FSL combustion chamber (12.5 m × 12.5 m × 22 m); the smoke ~~contained~~comprised a mixture of emissions from flaming and smoldering combustion.

2.1.1 Fuels

The fuel treatment during FLAME-4 has been described by Stockwell et al. (2014). In general, fuel samples were shipped to the FSL and stored from a few days to a few months with longer term storage occurring in a humidified refrigerator; instances identified where storage time may have influenced emissions are noted in Section 3.3. Prior to ignition, each fuel sample was arranged to promote burning under field-relevant conditions (e.g., grasses were standing upright instead of piled). Emissions were sampled from fires of six different globally relevant fuels: black spruce (BS), ponderosa pine (PP), wiregrass (WG), giant cutgrass (CG), Chinese rice straw (RS), and Indonesian peat (IP).

~~2.1.1~~2.1.2 Fuel Selection

Black spruce (*Picea mariana*) and ponderosa pine (*Pinus ponderosa*) are coniferous trees native to North America. Black spruce is common throughout many fire-prone ecosystems in the ~~Boreal~~boreal forest of Canada and Alaska ~~(Cumming, 2001)~~(Cumming, 2001). The BS sample was obtained near Fairbanks, Alaska. Ponderosa pine forests are common throughout the western US/Canada and experience extensive prescribed burning and wildfire activity (e.g., ~~(Veblen et al., 2000)~~(Veblen et al., 2000)). The PP sample was obtained locally in Missoula, Montana. ~~Woody~~Intact boughs (woody material and needles) were burned in the FLAME-4 fires.

Both grassland fuels analyzed—giant cutgrass (*Zizaniopsis miliacea)* and wiregrass (*Aristida stricta*)—predominantly grow in the southeastern U.S. Prescribed burning is common throughout the SE US as a means of hazard reduction and reforestation ~~(Haines and Busby, 2001)~~(Haines and Busby, 2001). Although CG typically grows in fresh or brackish marshes, these grasslands are still susceptible to burning and prescribed fires are often used within these ecosystems ~~(Wade et al., 2000)~~(Wade et al., 2000). Wiregrass is a bunchgrass commonly associated with longleaf pine forest ecosystems throughout the southern coastal plains. These ecosystems have been shown to benefit from frequent prescribed burning (Brockway and Lewis, 1997).

Rice straw (*Oryza sativa*) is an agricultural waste product commonly burned throughout Asia to clear fields. The RS sample was obtained from China, where the majority of BB has been attributed to crop residue ~~(Streets et al., 2003)~~(Streets et al., 2003). A peat sample was also imported from Indonesia, where 80% of the peatlands in Southeast Asia are located ~~(Chang and Song, 2010)~~(Chang and Song, 2010). Extensive deforestation and drainage of peatlands throughout Indonesia have greatly increased the susceptibility of peat to fire activity ~~(Heil, 2007)~~(Heil, 2007). Because peat deposits can be very deep and may smolder for months at a time ~~(Heil, 2007)~~(Heil, 2007), peat fires can be a major source of pollution to the atmosphere (Page et al., 2002).

~~2.1.2~~2.1.3 ATD Cartridge Samples

Adsorption/thermal desorption (ATD) cartridges were used to collect gaseous NMOCs. The cartridges were 8.9 cm long × 0.64 cm o.d. stainless steel tubes with an inert, internal SilcoTek coating; each contained a dual-sorbent bed composed of 100 mg Tenax TA 35/60 and 200 mg Carbograph 1 TD 60/80 in series (Camsco, Inc., Houston, TX). The use of multiple sorbents permits compounds with a wide range of volatilities to be collected ~~(Pankow et al., 2012)~~(Pankow et al., 2012). Prior to shipment to the field, each cartridge was conditioned at ~290 °C for 1 hour with a continuous flow of precleaned helium (~250 mL/min).

A glass-fiber filter coated with sodium thiosulfate was placed upstream of the cartridge in the sampling train to prevent particles and ozone from reaching the sorbent ~~(Helmig, 1997)~~(Helmig, 1997). In separate tests, these filters were found to scrub ozone at ~760 ppb with greater than 90% efficiency from ~3-L sample volume and were thus considered sufficient for removing the negligible ozone expected in fresh BB smoke (Akagi et al., 2013). A new filter was used with each sample. The filter holder, sampling line, and all fittings were Teflon. ~~Some adsorption of semi-volatile compounds to the tubing and filter may have occurred, though no corrections were applied.~~ Background samples were taken shortly before fire ignition. Smoke samples were collected after the smoke had equilibrated throughout the burn chamber. Breakthrough tests were conducted wherein two cartridges were placed in series to determine which compounds were incompletely trapped on a single cartridge. All sample volumes were ~~~2L~~2 L, with collection taking place over 15 min at a flow rate of ~150 mL/min. After sampling, the ATD cartridges were sealed with compression fittings using Teflon ferrules, and stored at <0 °C. The samples were analyzed within 1 month of sampling.

~~2.1.3~~2.1.4 Filter-Desorption Samples

To~~ further~~ characterize the volatilizable NMOCs that were not detected in the gas-phase cartridge samples, PM samples were collected on glass-fiber filters (0.7 µm pore size, ~8 L/min, ~60 min). Prior to shipment to the field, the glass-fiber filters were baked at ~130 °C for ~8 h. Following sample collection, the filters were immediately packaged in pre-baked aluminum foil and stored at <0 °C for up to one day prior to desorption. Volatilizable NMOCs were desorbed by passing clean N_2 through ~~the~~each filter (150 mL/min) at room temperature and trapped on an ATD cartridge. The clean N_2 source was supplied by scrubbing laboratory-grade N_2 with two ATD cartridges in series. Comparison of the data from the second scrubber cartridges with those from blank cartridges indicated that the contaminants in the N_2 carrier gas were effectively removed. As separate quality control tests, a blank filter and a background PM sample (collected in the burn chamber prior to ignition) were treated by the same desorption method. ~~The mass of~~Although the ~~background filter before and after PM collection~~QC tests indicated that ~~adsorbed species volatilized from the filter during sampling. Therefore the results from the~~ background PM was near zero, compounds detected in the BB filter desorption samples were not quantified~~ due to uncertainties in the masses of collected PM.~~. We report only the compounds identified from the filters that were not detected in the blank, background sample, or in the cartridge samples (with the exception of $\geq C_{14}$ hydrocarbons because they were detected in only one cartridge sample).

2.2 Chemical Standards

Calibration curves were determined for ~275 standard compounds in order to positively identify and quantify these components (listed in boldface in Table A1). Standards were prepared from: (1) a commercial mixture (PIANO mix, Sigma Aldrich, St. Louis, MO) containing ~140 compounds (alkanes, alkenes, and aromatic hydrocarbons) that was injected (5.0 µL) into a pre-cleaned and purged 2-L glass reservoir to produce a gas-phase standard; and (2) individual compounds dissolved in methanol. Seven standards (concentration levels) each were made from the PIANO mix and methanol solution. Each standard was injected onto an ATD cartridge and carried into the sorbent bed by a flow (~50-75 mL/min) of precleaned helium.

Initial analyses of the PIANO standards indicated that alkanes $>C_{10}$ remained partially adsorbed to the walls of the glass reservoir. To determine appropriate corrections, the PIANO standards were analyzed using a GC×GC instrument with flame ionization detection (FID). Because mass-based FID response factors (RF, area counts/ng) are approximately independent of carbon number ~~(Tong and Karasek, 1984)~~(Tong and Karasek, 1984), the GC×GC/FID data were used to estimate the mass percentage present in the gas phase at the time of cartridge spiking for each of the $>C_{10}$ alkanes by comparison to the average RF measured for C_7-C_9 alkanes. The measured gas-phase percentages ranged from ~96% for decane to ~33% for pentadecane. The adjusted mass amounts were used in the GC×GC/TOFMS calibration curves.

2.3 ATD Cartridge Analyses

Samples and standards were analyzed using a Pegasus 4D GC×GC/TOFMS (Leco Corp., St. Joseph, MI). Each ATD cartridge was desorbed using an ATD 400 system (Perkin-Elmer, Waltham, MA) connected to the GC×GC injection port via a fused silica transfer line at 225 °C. The flow direction through the cartridge during desorption was the reverse of that for sampling to prevent lower volatility analytes from contacting the Carbograph sorbent. Each cartridge was desorbed (285 °C, 10 min, 40 mL/min) onto a Tenax focusing trap (-20 °C). That trap was then desorbed (300 °C, 3 min) to transfer the analytes to the GC×GC injection port. The injection split ratio was 10:1. ~~The GC×GC~~ The analytical column set included a DB-VRX primary column (30 m, 0.25 mm I.D., 1.4 µm film, Agilent, Santa Clara, CA) and a Stabilwax secondary column (1.5 m, 0.25 mm I.D., 0.5 µm film, Restek, Bellefonte, PA). The GC×GC/TOFMS conditions are summarized in Table 1.

Samples were processed using the ChromaTof software package (Leco Corp., St. Joseph, MI). A peak was discarded if its area was <200,000 units or if the mass spectral match similarity relative to the NIST mass spectral database was <750 (out of 1000). The concentration of each compound measured in the corresponding background sample was subtracted from the ~~amount found~~concentration determined in the smoke sample. For the ponderosa pine and Indonesian peat smoke samples, background samples were unavailable; the background measurements for the other four samples were averaged and applied instead. ~~Standard~~For these two fuels, standard deviations were applied as the uncertainty in the average background concentrations; among the four background samples, concentrations varied ~10-160% of the average. ~~Chromatographic peaks~~Compounds were removed from consideration if ~~they did not survive background subtraction or~~ their concentrations were negative or not ~~statistically~~significantly different from zero ~~after~~following background subtraction.

Cases of ambiguous isomer assignments (because an authentic standard had not been used) were based whenever possible on published retention indices (e.g., ~~(Sojak et al., 1984; Sojak et al., 1973; Stein, 2013)~~(Sojak et al., 1984; Sojak et al., 1973; Stein, 2013)).

Otherwise, peaks were characterized here solely by chemical formula as assigned by the best mass spectral match(es).

Each positively identified compound (i.e., standard available) was quantified using calibration curves~~; tentatively~~. Tentatively identified analytes were quantified using the calibration curve of the most chemically similar standard compound~~.~~, as determined by comparing functional groups, carbon number, degree of unsaturation/conjugation, and aromaticity. Given the large number (~275) and wide range (Table A1) of standard compounds analyzed in this work, reasonable surrogate standard compounds were available for most of the compounds detected in the biomass burning samples. With a few exceptions (noted below), all components were calibrated using the deconvoluted total ion current. For analytes whose peak areas were low ~~relative to the *y*-intercept of the~~ (calibration ~~regression line, it was necessary to use~~curves yielded negative concentrations), RFs (area counts/ng) were used instead~~. Generally, the average RF of the three lowest concentration standards was used.~~ Error bars were calculated from the standard error in the linear regression of the calibration curve or the standard deviation of the average RF. The uncertainty for positively (tentatively) identified compounds was set to a minimum of 20% (50%). Mixing ratios used in determining emission factors (see Section 3.2) were calculated using the ambient temperature and pressure measured in the burn chamber. For the benzene and toluene peaks in some cartridge samples, the MS detector was saturated for the major ions in the mass spectra; thus these compounds were quantified using a minor ion. The same approach was required for camphene in the black spruce cartridge sample. The reported values for these species likely reflect lower limits due to the limited dynamic range.

3 Results & Discussion

3.1 Scope of the GC×GC Data

The GC×GC/TOFMS chromatograms of the cartridge samples from the six burns, highlighting the complexity of BB emissions, are shown in ~~Figures~~Figs. 1-6; the compounds detected are listed in Table A1~~.~~ (and in spreadsheet format in Table S1). The data have been organized into major chemical classes (panel b of Figs. 1-6 and Table A1). For reference, an example chromatogram highlighting regions of the major chemical classes is included in the Supplementary Material. Compounds with a wide range of volatilities and functionality were detected, from C_3 polar compounds through C_{15} hydrocarbons (Table A1). The range of detectable compounds was limited by the cartridge sampling and analysis conditions.

~~Lower volatility~~Sesquiterpenes (p_L^o ~1×10^{-3} kPa at 25 °C (Helmig et al., 2003)) were among the least volatile compounds ~~were not well characterized by this approach. Such~~ observed. Less volatile and/or more polar compounds may ~~be~~have adsorbed ~~by~~to the filter used upstream of the sampling cartridge to remove particles and ozone~~. Additionally~~. In addition to potential sampling losses, highly polar gases are not amenable to ~~analysis~~determination by GC. For instance, analysis of standards demonstrated that hydroxy phenols (e.g., resorcinol) did not elute from the column set used for this work. Further, with the Stabilwax secondary column utilized, several polar compounds (e.g., phenols and furfurals) ~~-~~“wrapped-around” (i.e., did not elute within one modulation period). Such peaks are thus very broad in the second dimension and may also appear in regions of the chromatogram typical of significantly less polar compounds. These features are most pronounced for the RS sample (~~Figure 5), which contained the highest fraction of oxygenated compounds.~~Fig. 5), which contained the highest fraction of oxygenated compounds. Such wrap-around effects should not have influenced the quantification of the positively identified compounds because these effects were captured in the calibration curves. For a limited number of compounds, wraparound may have influenced quantifications of tentatively identified compounds that wrapped-around and were quantified with a surrogate standard compound that did not (or vice versa).

On the high end of the volatility range, we have omitted all compounds eluting before 3-methyl-1-butene~~,~~ (p_L^o 120 kPa at 25 °C (Linstrom and Mallard, 2014)), the earliest eluting C_5 hydrocarbon (HC). HCs ≤C_3 were not trapped by the Tenax/Carbograph cartridges. Although C_4 HCs were detected, they displayed high breakthrough; the lightest standard (C_5) HC compounds exhibited minimal breakthrough and thus could not be used to quantify the observed C_4 compounds. Light (≤C_4) HCs have been previously shown to dominate the overall HC emissions from BB ~~(e.g., (Schauer et al., 2001;~~ (Schauer et al., 2001; Akagi et al., 2011)~~),~~, however these components have been generally well characterized by other methods (e.g., canister samples ~~(Simpson et al., 2011)~~(Simpson et al., 2011)) and typically are not significant precursors to atmospheric SOA ~~(Seinfeld and Pankow, 2003)~~(Seinfeld and Pankow, 2003).

Although several reported oxygenated compounds displayed high breakthrough as well, appropriate standard compounds allowed reasonable quantification. For such compounds, the corresponding standards showed evidence of breakthrough based on the GC×GC/FID data; thus application of the calibration curve somewhat corrects for the low trapping efficiency. However, comparison with co-located measurements (not shown) indicates that our measured concentrations of acetone and acetonitrile were comparatively low and therefore values reported here should be considered a lower limit. The same may be true of acrolein, although quantified co-located measurements were not available to verify the results. Such compounds are listed in italics in Table A1. Furan also displayed very poor trapping efficiency in the samples and standards. However, tests showed that the breakthrough was quite consistent and application of the calibration curves yielded results in good agreement with co-located measurements; thus we expect the reported values of furan to be accurate. A full comparison of all FLAME-4 NMOC measurements will be presented in a future publication.

3.2 Emission Factors

Emission factors (EF, g/kg of dry fuel burned) were calculated by the carbon mass balance method (~~Yokelson et al., 1999~~Yokelson et al., 1999; Stockwell et al., 2014):

$$\cancel{\mathrm{EF}_X = \mathrm{F}_C}\mathrm{EF}_X = F_\mathrm{C} \times \cancel{\frac{\mathrm{MM}_X}{\mathrm{MM}_C}} \frac{\mathrm{MM}_X}{\mathrm{MM}_\mathrm{C}} \times \cancel{\frac{\frac{\Delta X}{\Delta \mathrm{CO}_2}}{\sum_i^n\left(\mathrm{NC}_i \times \frac{\Delta Y_i}{\Delta \mathrm{CO}_2}\right)}} \frac{\frac{\Delta X}{\Delta \mathrm{CO}_2}}{\sum_i^n\left(\mathrm{NC}_i \times \frac{\Delta Y_i}{\Delta \mathrm{CO}_2}\right)} . \quad (1)$$

F_C is the mass fraction (g/kg) of carbon in the dry fuel and was measured for each fuel by an independent laboratory ~~for each fuel~~ (Table A1). MM_X and MM_C are the molar masses of compound X and carbon, respectively. ΔX is the background-subtracted ("excess") mixing ratio of compound X; $\Delta X/\Delta \mathrm{CO}_2$ (or $\Delta Y/\Delta \mathrm{CO}_2$) is the emission ratio (ER) of compound X (or Y) relative to CO_2 (ERs are also commonly referenced to CO for smoldering compounds). NC_i is the number of carbon atoms in compound Y_i. The summation represents the total carbon emitted during combustion, assuming complete volatilization; it includes CO_2, CO, and $\mathrm{C}_{1\text{-}3}$ alkanes/alkenes, as measured by open-path Fourier-transform infrared spectroscopy (OP-FTIR) ~~(Stockwell et al., 2014)~~(Stockwell et al., 2014) and averaged over the corresponding cartridge sampling periods. Strictly speaking, the summation should also include minor NMOCs and particulate carbon, however ignoring these components introduces errors on the order of only a few percent ~~(Yokelson et al., 2013)~~(Yokelson et al., 2013), which is well within the reported uncertainties.

The fire-integrated modified combustion ~~efficiency (MCE~~efficiencies (MCEs, $\Delta CO_2/(\Delta CO_2 + \Delta CO)$) for the six burns are included in Table A1. MCE is a measure of the relative contributions of flaming and smoldering combustion ~~(Yokelson et al., 1996)~~(Yokelson et al., 1996). Higher values (approaching 0.99) are indicative of pure flaming combustion, whereas lower values (~0.8) indicate pure smoldering combustion. Intermediate values reflect a mix of flaming and smoldering combustion.

MCEs and EFs for the PP and BS burns were compared to those presented by ~~Yokelson et al. (2013)~~Yokelson et al. (2013) for coniferous canopy fires. The MCEs in this work (PP, 0.927 and BS, 0.933) are similar to that reported by ~~(Yokelson et al., 2013)~~(Yokelson et al., 2013) (0.925 ± 0.036). In a correlation plot, the EFs for 48 overlapping compounds (Figure 7) are scattered about the 1:1 line, demonstrating that there was no systematic difference in these laboratory measurements relative to ~~Yokelson et al. (2013)~~Yokelson et al. (2013). Of the disparate points, several reflect monoterpene isomers, whose emissions can vary significantly among different plant species (see Section 3.3.5).

The MCE of the IP burn (0.832) in this work ~~(0.832)~~ was nearly identical to a laboratory IP burn ~~of Christian et al. (2003)~~ (0.838~~).~~) of Christian et al. (2003). However, the calculated EFs for IP smoke (Table A1) are ~2-7-fold lower than those reported by ~~Christian et al. (2003)~~Christian et al. (2003) for the 6 overlapping compounds. For comparison, the EFs based on OP-FTIR measurements for the FLAME-4 IP burns ~~(Stockwell et al., 2014)~~(Stockwell et al., 2014) averaged ~9-fold lower to ~3-fold higher than those by ~~Christian et al. (2003).~~Christian et al. (2003). The differences in measured EFs likely ~~arise~~arose from the different peat samples: the FLAME-4 peat sample was obtained from a previously burned/logged peat forest in Kalimantan, whereas the peat burned by ~~Christian et al. (2003)~~Christian et al. (2003) came from Sumatra. Given the wide variability in reported EFs, additional measurements of Indonesian peat fire emissions should be undertaken to help constrain their EFs. ~~Christian et al. (2003)~~Christian et al. (2003) have also reported emissions from Indonesian RS. The MCE during their burn (0.811) was much lower than that of the Chinese RS fire measured in this study (0.942); thus the ~~emissions of~~compounds emitted from smoldering ~~compounds~~combustion were significantly higher in the ~~Christian et al. (2003)~~Christian et al. (2003) study. The different combustion conditions were largely due to the fuel orientations. In the study by ~~Christian et al. (2003)~~Christian et al. (2003), RS was burned in a dense pile, as often occurs in non-mechanized agriculture. The FLAME-4 RS sample was burned as unpiled field residue, for which a similar MCE of ~0.93 has been measured for RS under ambient burn conditions ~~(Oanh et al., 2011)~~(Oanh et al., 2011). The relative importance of these two orientations is not well known (Akagi et al., 2011).

For the WG and CG fires, there are no available emission measurements for compounds that can be compared with our data.

3.3 NMOC Observations

Including NMOC emissions from all six burns, a total of ~~688~~674 compounds were positively or tentatively identified in the gas-phase cartridge samples (Table A1) and a further 34 compounds were identified solely in the filter-desorption samples (Table 2). Of ~~these~~the compounds observed in the cartridge samples, ~30-50% were positively identified across the six burns. There was significant variation in the number of compounds detected in each smoke sample, ranging from 129 (WG) to 474 (PP) (Table A1). The grass fires produced the fewest compounds, as well as the lowest overall NMOC emissions, with total EFs of 1.42 and 1.~~08~~07 g/kg for CG and WG, respectively, compared to 3.~~36~~37-14.~~57~~6 g/kg for the other fuels (Table A1). The lower emissions cannot be explained~~ entirely~~ by differences in combustion efficiency because the MCE of the CG fire was similar to those from the coniferous fuels, which displayed ~6-8-fold higher total EF (Table A1).

Abundant isomers were present in nearly all chemical classes, for example: 17 $C_{10}H_{14}$ isomers (aromatic HCs), ~~31~~29 C_7H_{12} isomers (aliphatic HCs), 38 $C_{10}H_{16}$ isomers (monoterpenes), and ~~13~~12 C_5H_8O isomers (aldehydes and ketones) were detected. Because chemical structure significantly influences chemical reactivity ~~(Ziemann and Atkinson, 2012)~~(Ziemann and Atkinson, 2012), it is advantageous to speciate the compounds in these groups to better predict BB plume chemistry. Although in many cases specific structures could not be assigned, future availability of additional standard compounds will enable more thorough chemical identification.

Of the ~~688~~674 compounds detected, only ~~75~~78 compounds were present in all ~~6~~six cartridge samples (~~Figure~~Fig. 8). Most of these were 'major' compounds, defined as EF > 0.01 g/kg in any sample (e.g., benzene, toluene, and furan). These major compounds accounted for ~~55-81~~57-84% of the total EF from the burns. Efforts aimed at improving the representation of BB SOA in atmospheric models might begin with this group. Of the ~~242~~210 compounds unique to a single burn, most were present at low levels ('minor', ~~Figure~~Fig. 8). Aliphatic HCs constituted approximately half of these ~~minor~~ compounds, due to the large ~~number~~numbers of potential isomers.

To more clearly show the relative proportions of the identified compounds, the data were sorted into groups based on functionality and carbon number (b panels, ~~Figures~~Figs. 1-6). Because these figures do not include compounds that were not~~ well~~ characterized by our approach (e.g., low molecular weight compounds known to have high emissions), they do not provide a full accounting of the NMOC emissions. A complete synthesis of the NMOC measurements during FLAME-4 is underway and will be presented in a separate study. Interesting features of each class elucidated by GC×GC/TOFMS, particularly as relevant for SOA formation, are described in the following sections.

3.3.1 Aromatic Hydrocarbons

Aromatic HCs represented a major fraction of emissions from all fuels (Figs. 1-6), except WG (only ~10~~%,~~% by EF, Fig. 4); for CG in particular, aromatic HCs were overwhelmingly dominant (~43~~%,~~% by EF, Fig. 3). The majority of the aromatic emissions were alkyl aromatic HCs, in terms of both EF and number of compounds (Table A1), although significant levels of compounds with unsaturated substituents (e.g., styrene, phenylacetylene and their substituted analogs) were also detected in the BS, PP, and CG burn emissions (~~Figures~~Figs. 1b-3b). In all cases, the most abundant aromatic HC was benzene, followed by toluene~~,~~ (Table A1), despite being under-~~predicted~~estimated by our measurements~~,~~ (Section 2.3); this is consistent with prior measurements of aromatic HCs in BB emissions (Akagi et al., 2011~~; Andreae and Merlet, 2001; Yokelson et al., 2013)~~; Andreae and Merlet, 2001; Yokelson et al., 2013). Further, higher molecular weight aromatic HCs were detected than are ~~usually~~typically reported ~~in gas-phase BB emissions. Many compilations report $\leq C_9$ aromatic HCs~~elsewhere (e.g., ~~propylbenzene isomers)~~$\leq C_9$, (Akagi et al., 2011~~; Andreae and Merlet, 2001)~~; Andreae and Merlet, 2001); more recently, ~~Yokelson et al. (2013) reported~~ unspeciated C_{11} alkyl aromatics~~.~~ (Yokelson et al., 2013)). In this work, a number of C_{11} isomers with substituents of varying double bond equivalents (DBE) (0-2) were detected (Table A1) and in the filter-desorption tests, benzene derivatives as large as nonyl benzene were observed (Table 2). Naphthalene and several methyl naphthalenes as well as related compounds such as biphenyl and acenaphthylene were detected in the emissions from all fuels. Higher molecular weight naphthalene derivatives and polycyclic aromatic HCs (PAHs) were tentatively identified in the filter-desorption samples, including a trimethyl naphthalene isomer and phenanthrene (Table 2).

The chemical structure of aromatic HCs may influence the kinetics and thermodynamics of SOA formation and will vary from plume to plume depending on the isomeric ratios. The atmospheric reactivity of aromatic HCs is dominated by OH addition, for which the reaction rate increases with the number of alkyl substituents and is further influenced by their position (~~(Ziemann and Atkinson, 2012)~~(Ziemann and Atkinson, 2012) and references therein). For ~~instance~~example, the rate constant of 1,3,5-trimethyl benzene is ~10x ~~faster~~higher than that of *n*-propyl benzene ~~(Finlayson-Pitts and Pitts, 2000)~~(Finlayson-Pitts and Pitts, 2000). However, similar SOA yields of ~30% (roughly independent of particle mass concentration) have been measured by ~~Ng et al. (2007)~~Ng et al. (2007) for benzene, toluene, and *m*-xylene under low NO_x conditions (significantly lower yields were observed under high NO_x conditions and varied as a function of particle mass concentration). Naphthalene and its derivatives exhibit notably higher SOA yields than the substituted benzenes: up to ~73% under low NO_x conditions and ~20-30% under high NO_x conditions ~~(Chan et al., 2009)~~(Chan et al., 2009). Because naphthalene and its derivatives composed up to 17% (CG) of total aromatic HCs, such compounds may be significant contributors to SOA mass in BB plumes (Chan et al., 2009).

3.3.2 Oxygenated Aromatic Compounds

Oxygenated aromatic compounds constituted between 3.8% (BS) to 17% (CG) of the total EF measured from each fuel. Phenol was the most abundant oxygenated aromatic species emitted for all of the fuels tested (Table A1). Several substituted phenols were also identified, including methyl and dimethyl phenols. Phenolic compounds arise from the pyrolysis of lignin, an amorphous polyphenolic polymer~~.~~ (Pandey and Kim, 2011). Guaiacol was the only methoxy phenol detected in the cartridge samples (Table A1); however, several guaiacol derivatives were volatilized from the filter samples, primarily from the coniferous fuels (Table 2). ~~Conifers are softwoods, which~~Guaiacols are commonly measured in smoke from coniferous fuels (Jiang et al., 2010; Saiz-Jimenez and De Leeuw, 1986), as these softwoods contain lignins composed primarily of guaiacyl units ~~(Shafizadeh, 1982)~~(Shafizadeh, 1982)~~; therefore the presence of many guaiacols is to be expected from such fuels (Jiang et al., 2010; Saiz-Jimenez and De Leeuw, 1986).~~. Several other nonphenolic oxygen-containing aromatic compounds were observed, including furans, aldehydes, ketones, and ethers (Table A1). Little information exists regarding the formation of such compounds in fires, although several have been previously observed in BB smoke (~~Yokelson et al., 2013~~Yokelson et al., 2013; Andreae and Merlet, 2001).

Phenol, alkyl phenols, and guaiacol have been shown to produce SOA in relatively high yields (~25-50%) from OH-initiated gas-phase chemistry ~~(Yee et al., 2013; Nakao et al., 2011)~~(Yee et al., 2013; Nakao et al., 2011). ~~Recently,~~Recent work has also demonstrated ~~Smith et al. (2014) observed~~ nearly 100% SOA yield from ~~the~~ aqueous-phase ~~reaction~~photochemical reactions of phenols ~~with excited state organic compounds.~~(Smith et al., 2014; Sun et al., 2010). Given the dominance of phenols among the oxygenated aromatic compounds (Figs. 1-6) and their reportedly high SOA yields, phenols are likely to be the most significant SOA precursors in this category. SOA formation from the less abundant oxygenated aromatic compounds (aldehydes, ketone, furans) has not been well characterized. However, benzaldehyde, acetophenone and benzofuran (including its methyl derivatives) were present in the smoke from all six burns; ~~thus~~ these compounds may be good subjects for future smog chamber studies.

3.3.3 Aliphatic Hydrocarbons

Approximately half of all detected compounds were aliphatic HCs, with 0-4 DBE. Up to 33% (IP) by EF of the aliphatic HC category is attributed to compounds larger than the $\leq C_8$ compounds typically reported in BB emissions (Akagi et al., 2011; ~~Andreae and Merlet, 2001~~Andreae and Merlet, 2001). Few BB studies have measured $>C_9$ aliphatic HCs. ~~Ciccioli et al. (2001)~~Ciccioli et al. (2001) detected up to C_{13} alkanes/alkenes from flaming and smoldering pine wood; ~~Schauer et al. (2001)~~Schauer et al. (2001) measured C_{1-9} and C_{18-24} alkanes in the gaseous emissions from pine wood burning, but they ~~do~~did not report the intermediate species. In four of the six FLAME-4 filter-desorption samples, tetradecane and pentadecane were observed (Table 2), suggesting that intermediate volatility compounds are often present in BB emissions. IP smoke contained the highest MW HCs of all burns with alkanes and 1-alkenes detected up to C_{18} (Tables A1 and 2). This is consistent with the relative MCEs (Table A1) because smoldering combustion tends to generate higher MW compounds ~~(Lobert and Warnatz, 1993).~~(Lobert and Warnatz, 1993).

Aliphatic HCs were well separated according to DBE; thus the relative contribution of saturated and unsaturated HCs can be readily assessed (Fig. 9). The CG fire emitted the highest fraction of unsaturated compounds, with only one alkane detected; in contrast, IP combustion led predominantly to saturated alkanes (Fig. 9, Table A1). Emissions for the other four fuels fell between CG and IP smoke, with three to eight times higher levels of 1-DBE compounds than saturated compounds (Fig. 9). Of the 1-DBE compounds, the most abundant isomers were generally 1-alkenes; at ≥C_{13}, 1-alkenes were often the only unsaturated compounds detected (Tables A1 and 2).

Whereas the aliphatic HC emissions from most fuels were composed primarily of 1- and 2-DBE compounds, 3-DBE compounds constituted the highest fraction of aliphatic HCs in the CG fire emissions (Fig. 9). This class was dominated by 1,3-cyclopentadiene and its methyl derivatives (Table A1). 1,3-Cyclopentadiene may form via loss of CO from phenol (a product of lignin pyrolysis, as discussed in Section 3.3.2) and is thought to contribute to the formation of PAHs (e.g., naphthalene) and similar compounds (e.g., indene) during combustion ~~(Fitzpatrick et al., 2008; Mulholland et al., 2000)~~(Fitzpatrick et al., 2008; Mulholland et al., 2000). This is consistent with the high relative contributions from phenolic compounds and PAHs in CG emissions (~~Figure~~Fig. 3) and suggests that CG has high lignin content (discussed further in Section 3.3.6).

Much recent research has probed the SOA formation potential of aliphatic HCs as a function of carbon number and structure. The SOA yield of alkanes increases dramatically with increasing carbon number—particularly for >C_{10} compounds ~~(Lim and Ziemann, 2009)~~(Lim and Ziemann, 2009); for example, yields of ~50% ~~(Presto et al., 2010)~~(Presto et al., 2010) to ~90% ~~(Lim and Ziemann, 2009)~~(Lim and Ziemann, 2009); have been reported for heptadecane in the presence of NO_x. Further, the SOA yields of linear alkanes are greater than branched alkanes ~~(Ziemann, 2011)~~(Ziemann, 2011)~~. Unsaturated aliphatic HCs are more reactive toward OH and nitrate radical than alkanes, and are susceptible to reaction by ozone. The SOA yield from 1-alkenes is generally higher than alkanes up to C_{12}, at which point the yield of 1-alkenes plateaus (Ziemann, 2011). Terminal alkenes generally exhibit higher SOA yields than internal alkenes, due to a greater propensity for the latter to fragment during oxidation .~~. Unsaturated aliphatic HCs are more reactive toward OH and nitrate radical than alkanes, and are susceptible to reaction by ozone (Atkinson and Arey, 2003b). The SOA yields from 1-alkenes are ~17-117% higher than alkanes up to C_{13}, at which point the yields of 1-alkenes plateau ~~(Ziemann and Atkinson, 2012; Matsunaga et al., 2009)~~(Ziemann, 2011; Lim and Ziemann, 2009)~~.~~. Terminal alkenes exhibit ~20-380% higher SOA yields than internal alkenes, due to a greater propensity for the latter to fragment during oxidation (Ziemann and Atkinson, 2012; Matsunaga et al., 2009). The aliphatic HC isomers most likely to generate significant SOA (i.e., *n*-alkanes and 1-alkenes) were those predominantly observed in the sampled BB emissions: of the non-grass fuels (the grasses did not contain significant intermediate volatility aliphatic HCs), the fraction (by EF) of ~~$\geq C_{10}$~~linear alkanes ~~that are linear~~ ($\geq C_{10}$) ranged from 68% (IP) to 87% (BS) and the fraction of ~~$\geq C_{10}$ alkenes with a~~ terminal ~~double bond~~alkenes ($\geq C_{10}$) varied from 59% (IP) to 93% (BS) (Table A1).

3.3.4 Oxygenated Aliphatic Compounds

The relative contributions of oxygenated aliphatic compounds to the measured total EF from each burn varied by fuel, from ~10% for IP to ~31% for WG and RS. For the compounds detected here, the dominant oxygenated compounds across all fuels were low MW ketones and aldehydes (~~Figures~~Figs. 1-6). These emissions include acyclic compounds, as well as many cyclopentenone derivatives, and cyclopentene-dione isomers (Table A1). Such compounds can arise from the pyrolysis of glucose (Paine et al., ~~2008a~~2008b).

RS emissions were dominated by oxygenated compounds~~ (Fig. 5),~~, which can be readily observed in Fig. 5 by the broad smearing of polar compounds along the secondary axis of the chromatogram. Interestingly, the RS sample had the highest ash content of all fuels tested (7.7% vs. 1.5-3.8% by weight; Table A1). Pyrolysis experiments have demonstrated that ash can catalyse cellulose degradation leading to greater yields of several light oxygenated compounds ~~(Patwardhan et al., 2010; Eom et al., 2013; Eom et al., 2012)~~(Patwardhan et al., 2010; Eom et al., 2013; Eom et al., 2012), including hydroxyacetone whose EF is ~10-fold higher from RS than any other fuel (Table A1). Thus the ~~disproportionately~~ high ash content in RS may explain the preponderance of the light oxygenated compounds in the BB emissions from this fuel.

Several of the identified ketones and aldehydes are known SOA precursors, such as methyl vinyl ketone ~~(Chan et al., 2013; Liu et al., 2012)~~(Chan et al., 2013; Liu et al., 2012) and methacrolein ~~(Chan et al., 2010; Surratt et al., 2006)~~(Chan et al., 2010; Surratt et al., 2006). Methacrolein and other unsaturated aldehydes observed in the cartridge samples (e.g., 2-butenal; Table A1) have been shown in laboratory studies to produce SOA through peroxy acyl nitrate (PAN) intermediates, with SOA yields ~~increasing~~that increase with increasing NO_2/NO ratios ~~(Chan et al., 2010)~~(Chan et al., 2010). At the NO_2/NO EF ratios of ~3.5-7 reported ~~from~~for ambient BB (Akagi et al., 2013~~; Simpson et al., 2011)~~; Simpson et al., 2011) the SOA yield of methacrolein, for example, is~~ reportedly~~ ~19-24% compared to <3% under high NO conditions ~~(Chan et al., 2010)~~(Chan et al., 2010)~~. Further, ~40% of NO_x has been observed to rapidly form PANs in boreal fire plumes (Alvarado et al., 2010)~~. These observations suggest that unsaturated aldehydes have the potential to form significant SOA via the PAN pathway in BB smoke. Although the available SOA yields of oxygenated aliphatic compounds are generally relatively low (<10%), the generated SOA mass may not be trivial in smoke plumes with a high fraction of oxygenated aliphatic compounds (e.g., as from RS).

3.3.5 Terpenoids

Figures 1b and 2b illustrate the significant levels of terpenoids detected in smoke from both coniferous fuels (BS, 27% and PP, 14~~%).~~% by EF). The relative contributions of terpenoids from the other fuels were small, and were dominated by isoprene. Isoprene was the only terpene detected in the smoke of all plant fuels sampled (Table A1). Detection of isoprene from burning peat and non-isoprene emitting plants such as RS ~~(Kesselmeier and Staudt, 1999)~~(Kesselmeier and Staudt, 1999) indicates that isoprene is formed during combustion.

Terpenoids constituted the largest EF category in BS smoke~~ by EF~~, but only the fourth largest in PP (~~Figures~~Figs. 1 and 2). The BS sample was cut a few days prior to burning and thus should ~~be~~have been representative of living BS trees. In contrast, the PP branches were cut approximately one month before the burn and included a mix of brown and green needles~~.~~ at the time of burning. The PP sample therefore ~~represents~~represented a mix of forest floor litter and fresh, live branches. Some losses (e.g., through volatilization) of biogenic compounds ~~may have~~likely occurred while storing the PP sample. A more rigorous comparison of the relative magnitudes of terpene emissions should ideally utilize branches of similar freshness. However, both fresh and aged needles (litter) can be important fuel components of fires in coniferous ecosystems ~~(Stockwell et al., 2014; Yokelson et al., 2013)~~(Stockwell et al., 2014; Yokelson et al., 2013); the data reported thus are useful for understanding the smoke from such fires.

In this study, 32 monoterpene (MT) isomers were detected in the smoke from each coniferous fire, of which 13 were positively identified (Table A1). ~~Prior to this work Ciccioli et al. (2001)~~Prior to this work, Ciccioli et al. (2001) presented the most comprehensive list of MTs from BB, reporting 14 MTs during a laboratory burn of *Pinus pinea* using GC/MS. In FLAME-4, the 10 most abundant MTs represented ~90% of the total MT emissions for each coniferous fuel, including many of the compounds measured by ~~Ciccioli et al. (2001)~~Ciccioli et al. (2001). Consistency in the MT emissions from a given plant species is suggested by the similarity in the MT-isomer distribution from the BS fire emissions shown in ~~Figure~~Fig. 10 and a separate BS fire (see ~~Figure~~Fig. S2). The relative proportions of the top 10 MT isomers from each fuel are shown in ~~Figure~~Fig. 10, compared to those previously measured in the corresponding plant essential oils ~~(Krauze-Baranowska et al., 2002; Anderson et al., 1969; von Rudloff, 1975)~~(Krauze-Baranowska et al., 2002; Anderson et al., 1969; von Rudloff, 1975). Camphene (3-carene) is the dominant MT isomer in BS needles (wood), whereas β-pinene (3-carene) is the dominant MT isomer in PP needles (wood) (Fig. 10). Although there is quite reasonable agreement between the MT composition of essential oils and the smoke samples from the coniferous fuels, the relative proportions of MTs in the smoke samples are not exact matches to the essential oils. First, the distribution of MTs differs considerably between the needle- and wood- derived essential oils of these conifers; for example 3-carene is significantly higher in wood than needles (~~Figure~~Fig. 10). The relative mass of needles vs. wood burned in these experiments was not measured, but visual observations indicated that needle combustion dominated~~.~~ (most of the needles burned, but much of the wood was only charred). This is consistent with the measured distribution of MT isomers in the needle and twig-derived essential oils (e.g., comparing camphene and 3-carene in BS smoke). Further, it is known that MTs can thermally isomerize during pyrolysis (~~(Stolle et al., 2009)~~(Stolle et al., 2009) and references therein). In particular, myrcene and limonene are known thermal rearrangement products of β-pinene ~~(Stolle et al., 2009)~~(Stolle et al., 2009). This may explain the lower relative concentration of β-pinene and higher relative proportions of myrcene and limonene in PP smoke compared to the MT distribution of needle and wood essential oils.

The similarities between the MTs in smoke and those in essential oils demonstrate that MT emissions from BB are plant specific. Because terpenes are essentially distilled out of storage reservoirs during fires ~~(Yokelson et al., 1996)~~(Yokelson et al., 1996), essential oils obtained by steam distillation are likely to be good proxies when predicting MT emissions from BB. For example, the BS essential oil data ~~(von Rudloff, 1975)~~(von Rudloff, 1975) were also useful for confirming the identification of monoterpenoids detected in BS smoke, including bornyl acetate ($C_{12}H_{20}O_2$) and santene (C_9H_{14}) (Table A1). Although only two coniferous fuels were examined in this work, the major MTs (limonene and α-pinene) observed by ~~Ciccioli et al. (2001)~~Ciccioli et al. (2001) are also in agreement with the major constituents of *Pinus pinea* essential oil ~~(Nasri et al., 2011)~~(Nasri et al., 2011). Although promising, the reproducibility of such ~~correlations~~similarities should be confirmed by testing a wider range of plant species and burn conditions.

Given the wide range of atmospheric reactivity and SOA yields among the MT isomers ~~(Lee et al., 2006; Atkinson and Arey, 2003)~~(Lee et al., 2006; Atkinson and Arey, 2003a), the variability in MT isomers emitted from different plant species could significantly impact BB SOA chemistry. ~~The compounds included in Figure 10 have been arranged in order of increasing SOA yields, based largely on Lee et al. (2006)~~The compounds included in Fig. 10 have been arranged in order of increasing SOA yields, based largely on Lee et al. (2006) for reaction with OH. As discussed by Akagi et al. (2013), reaction with OH is likely the dominant MT oxidation pathway in smoke plumes. The SOA yield for reaction of camphene with OH has not been characterized; however its SOA yield with ozone is reportedly negligible ~~(Hatfield and Hartz, 2011)~~(Hatfield and Hartz, 2011). Tricyclene does not contain double bonds; its SOA formation potential is assumed here to be the lowest of the MT isomers. Although 1.4× higher total MT EFs were observed for BS (Figs. 1 and 2), BS smoke contained predominantly low SOA-yield MTs, whereas PP-derived smoke contained higher SOA-yield MTs (~~Figure~~Fig. 10). For comparison, ~~Figure~~Fig. 10 also ~~presents~~includes the relative MT EFs for “coniferous canopy” fuels listed in ~~the compilation by Yokelson et al. (2013)~~Yokelson et al. (2013). The average “coniferous canopy” values do not adequately represent the distribution of either BS or PP, particularly the contributions of the high SOA-yield species, such as limonene. More accurate model predictions of MT-derived SOA likely will be achieved with knowledge of the actual distribution of MT isomers emitted in BB smoke, which will vary among different plant species. At least for MTs, utilizing regional averages ~~or relying solely on PTRMS measurements~~ may not be sufficient for representing SOA formation in air quality and climate applications. ~~Prediction~~Considering the wide range of reported SOA yields among the MT isomers (<10-60% (Lee et al., 2006; Griffin et al., 1999)), prediction errors may be significant considering the large contribution and distribution of these species in the smoke of coniferous fuels (~~Figures~~Figs. 1 and 2). In the absence of speciated MT measurements, we propose that SOA models~~ that~~ apply the MT distribution from needle-derived essential oils corresponding to the vegetation mix (if available) ~~will generally~~to yield more reliable results than ~~models~~ assuming a single ~~lumped~~surrogate MT. In this regard, measured or modeled total MT EF could be distributed over the relative proportions of specific isomers reported for plant-specific steam-distilled essential oils.

~~Limited information has been reported regarding the speciation of sesquiterpenes (SQTs) in BB smoke. Ciccioli et al. (2001) detected four SQT isomers from burning *Pinus pinea*, but only aromadendrene was identified. Other reports of SQTs in BB smoke are typically derived from PTRMS measurements (e.g.,~~ Limited information has been reported regarding the speciation of sesquiterpenes (SQTs) in BB smoke. Ciccioli et al. (2001) detected four SQT isomers from burning *Pinus pinea*, but only aromadendrene was identified. Other reports of SQTs in BB smoke are typically derived from proton-transfer reaction mass spectrometry (PTRMS) measurements (e.g., ~~(Yokelson et al., 2013)~~(Yokelson et al., 2013)), and thus do not provide structural information. SQTs have historically been difficult to measure ~~due to their relatively low volatilities and high reactivities (Pollmann et al., 2005;~~ (Pollmann et al., 2005; Bouvier-Brown et al., 2009)~~. However, Pollmann et al. (2005) found no significant adsorption losses of SQTs to a thiosulfate-impregnated filter, as well as high recovery of all isomers from Tenax TA sorbent cartridges. Therefore, SQT-related sampling artifacts were likely minimized in the sampling configuration used in this work, although losses to the Teflon sampling line were not characterized. Highly reactive SQTs may have been partially lost if ozone was not completely removed (Pollmann et al., 2005); however that is unlikely given the negligible ozone concentrations present in fresh BB smoke (Yokelson et al., 2003; Akagi et al., 2013).~~

~~Eleven SQT isomers were detected in smoke from the coniferous fuels (Table A1). These GC×GC measurements therefore reflect the most comprehensive characterization of SQTs in BB smoke to date.~~ due to their relatively low volatilities (p_L^{o} ~1×10^{-3} kPa at 25 °C (Helmig et al., 2003)) and high reactivities (atmospheric lifetimes on the order of minutes to hours (Atkinson and Arey, 2003a)). In this work, efforts were made to minimize SQT-related sampling artifacts. Relevant to our sampling configuration, Helmig et al. (2004) found high (~90%) recoveries for sesquiterpenes following nearly 4 m of Teflon tubing. Further, Pollmann et al. (2005) found no significant adsorption losses of SQTs to a thiosulfate-impregnated filter, as well as high recovery of all isomers from Tenax TA sorbent cartridges. Highly reactive SQTs may have been partially lost if ozone was not completely removed

(Pollmann et al., 2005); however that is unlikely given the near-zero ozone concentrations present in fresh BB smoke (Yokelson et al., 2003; Akagi et al., 2013) and the ozone-removal efficiency of the sodium thiosulfate-impregnated filters (Section 2.1.3).

Eleven SQT isomers were detected in smoke from the coniferous fuels (Table A1). These GC×GC measurements therefore reflect the most comprehensive characterization of SQTs in BB smoke to date. No SQTs were found in smoke from the other fuels, however the IP fire emitted SQT-like compounds with the formula $C_{15}H_{26}$ (Table A1). ~~Sesquiterpenes~~SQTs constituted a small fraction of the terpenes observed in both BS and PP (~~Figures~~Figs. 1 and 2), consistent with the relatively low levels present in these essential oils ~~(Krauze-Baranowska et al., 2002; von Rudloff, 1975)~~(Krauze-Baranowska et al., 2002; von Rudloff, 1975). The majority of the observed SQTs are tentatively identified as isomers of cadinene, amorphene, and/or muurolene, which have the same bi-cyclic cadalane skeleton and differ only in the position of the two double bonds and stereochemistry; these are labelled as cadinene isomers in Table A1. Cadinene isomers have been previously detected in the essential oils of BS ~~(von Rudloff, 1975)~~(von Rudloff, 1975) and PP ~~(Krauze-Baranowska et al., 2002)~~(Krauze-Baranowska et al., 2002). Other tentatively identified compounds with a cadalane backbone were also observed, including copaene ($C_{15}H_{24}$), calamenene ($C_{15}H_{22}$), and calacorene ($C_{15}H_{20}$) (Table A1). Cadinenes have received comparatively little study in terms of atmospheric reactivity; however other SQT isomers are known to have high SOA yields ~~(Lee et al., 2006)~~(Lee et al., 2006).

3.3.6 Furans

Although furans are oxygenated aromatic species, a separate class was created since they constituted a significant fraction (5-37~~%)~~% by EF) of the smoke from each fuel tested (~~Figures~~Figs. 1-6). Furans arise primarily from the breakdown and dehydration of cellulose ~~(Paine et al., 2008b).~~(Paine et al., 2008a). Compounds in this group generally contained 4-6 carbons with alkyl and/or oxygenated substituents, most commonly as aldehyde or alcohol moieties (Table A1). Furan emissions were generally dominated by furan and furfural, with significant contributions from 2-methyl furan and 2-furanmethanol (Figs. 1-6, Table A1).

Wiregrass smoke contained the highest relative furan contribution (37~~%,~~% by EF, Fig. 4). Furfural was the dominant species emitted from this fuel within the range of analyzed compounds (Table A1). In contrast, CG combustion emitted largely benzene and naphthalene derivatives (~~Figure~~Fig. 3). The variation in emissions could indicate substantial differences in the structure of these grasses: the high levels of furans detected in WG smoke ~~suggests~~suggest high levels of cellulose in the plant material whereas the preponderance of aromatic compounds, including phenols, in CG smoke suggest high lignin content as discussed above (Section ~~3.3.1). This~~3.3.2). Although the biomass composition of these grasses has not been reported, this hypothesis is consistent with the structures of these plants. Giant cutgrass is characterized by tall, wide, and stiff leaves (USDA, 2014) that likely require higher lignin content for support. In comparison, wiregrass is short, wiry, and ~~flimsy. Although the biomass composition of these grasses have not been measured, Ortega et al. (2013) reported that the fraction of particle-phase levoglucosan (as f_{60} in their aerosol mass spectrometry measurements)—a known product in cellulose degradation—was higher in WG smoke than other fuels tested except sawgrass, consistent with the hypothesis of high cellulose content in WG.~~ pliable (USDA, 2014). The MCEs were quite different for these two burns (0.925 for CG vs. 0.97 for WG) and thus combustion conditions may also have influenced the emitted compounds.

Furans are highly reactive, with atmospheric lifetimes on the order of several hours with respect to OH oxidation (Bierbach et al., 1992). Although the kinetics of furfural oxidation have been characterized ~~(Colmenar et al., 2012~~(Colmenar et al., 2012; Bierbach et al., 1995), product studies have not yet been conducted, thereby limiting assessment of its SOA-formation potential. Gas-phase photochemistry of alkyl furans has been more extensively studied (Alvarado et al., 1996~~; Aschmann et al., 2011;~~ ; Aschmann et al., 2011; Bierbach et al., 1992~~; Gómez Alvarez et al., 2009)~~; Gómez Alvarez et al., 2009) and generally proceeds via OH-radical addition to the aromatic ring with subsequent ring opening (Bierbach et al., 1995). The major identified products are unsaturated-1,4 dicarbonyls, with yields that decrease with increasing number of alkyl substituents ~~(Aschmann et al., 2014)~~(Aschmann et al., 2014)~~. Strollo and Ziemann (2013).~~. Strollo and Ziemann (2013) found that these first-generation reaction products of 3-methyl furan can undergo acid-catalyzed condensed-phase oligomerization reactions, with SOA yields up to 15%. Given that aldehydes are more likely to oligomerize than ketones ~~(Strollo and Ziemann, 2013)~~(Strollo and Ziemann, 2013), furan and 3-methyl furan will likely produce the highest SOA yields by this mechanism since their predominant first generation products are unsaturated dialdehydes ~~(Aschmann et al., 2014)~~(Aschmann et al., 2014). These unsaturated aldehydes may also react through a PAN channel, as discussed in Section 3.3.4. Given the high levels of furans detected in these smoke samples, it is important to elucidate the potential SOA formation pathways of these compounds and their role in SOA production in BB plumes.

3.3.7 Nitrogen- and sulfur-containing compounds

Emissions of N- and S-containing compounds are generally proportional to the nitrogen and sulfur content of the fuel biomass ~~(Ward, 1990).~~(Ward, 1990). Consistent with the relative nitrogen content in the fuels (Table A1), ~~giant cutgrass~~CG smoke had the highest relative contribution from N-containing species: 11% vs. ~2-6% from the other fuels. The predominant emitted N-species from CG combustion were nitriles that arise from the pyrolysis of amino acids ~~(Lobert and Warnatz, 1993).~~(Lobert and Warnatz, 1993). Interestingly, the predominant N-containing species from most other fuels ~~was pyrrole~~ were pyrroles rather than nitriles. However, acetonitrile was likely underestimated by our measurements due to high breakthrough. Extensive N-heterocyclic compounds have also been observed in PM samples from burns of RS ~~(Ma and Hays, 2008)~~(Ma and Hays, 2008) and PP ~~(Laskin et al., 2009)~~(Laskin et al., 2009), consistent with the observations herein. The SOA-formation potentials of pyrroles and ~~nitrile~~nitriles have not been elucidated. However, due to the small molecular sizes (<C_7) and relatively low concentrations of the observed compounds~~,~~ (~2-11% of the total EF), they are not likely to contribute significantly to BB SOA.

Sulfur is an important nutrient for plant ~~physiology~~function. As discussed by ~~Ward (1990)~~Ward (1990), sulfur in ecosystems can only be replenished through deposition; thus local losses of sulfur due to fire activity can influence land sustainability and sulfur transport. Dimethyl sulfide (DMS) and dimethyl disulfide are the predominant organosulfur compounds that have been reported in BB smoke to date (Akagi et al., 2011; Simpson et al., 2011; Friedli et al., 2001; Meinardi et al., 2003). Thiophene—the sulfur analog to furan—and its derivatives were detected in five of the fuels tested. ~~To our knowledge, only Ciccioli et al. (2001) have~~Ciccioli et al. (2001) have previously identified thiophene in BB emissions, however they do not report an EF. ~~Dimethyl sulfide (DMS) and dimethyl disulfide are the predominant organosulfur compounds that have been reported in BB smoke to date (Akagi et al., 2011; Simpson et al., 2011; Friedli et al., 2001; Meinardi et al., 2003).~~ In this work, the thiophene EF has been quantified, along with its methyl derivatives and benzo(a)thiophene ~~derivatives.~~(Table A1). The reported thiophene EFs are comparable to the EFs commonly reported for DMS (Akagi et al., 2011~~; Simpson et al., 2011)~~; Simpson et al., 2011), therefore thiophenes may be important organosulfur species in BB emissions. (Dimethyl disulfide was detected at trace levels in the RS burn, but was not quantified due to lack of a suitable standard compound.) Rate constants for reactions of thiophene with atmospheric oxidants have been measured ~~(Atkinson et al., 1983;~~ (Atkinson et al., 1983; Cabañas et al., 2005), and are generally ~~slower~~lower than for the corresponding furan reactions due to greater aromaticity of the thiophene ring compared to furan (Bierbach et al., 1992); SOA yields are unknown.

4 Conclusions

This work represents the first application of GC×GC/TOFMS for the broad characterization of NMOCs from biomass burning. Utilizing the approach described herein, ~~722~~708 total compounds in the C_2-C_{18} range were speciated, including the cartridge and filter-desorption samples, demonstrating the extensive capability of GC×GC/TOFMS to facilitate identification and quantification of BB emissions. Although the ability to reliably quantify analytes present at very high concentrations (e.g., benzene) was hindered due to limited dynamic range, newer model ATD instruments permit trapping of the unused portion of each sample, thereby enabling multiple analyses of each cartridge sample. In particular, application of different GC×GC inlet split ratios would extend the range of quantitation and different column sets could be used to target more or less polar species. Further, alternative sorbent beds could be utilized for ATD cartridge sampling to target different volatility ranges, as desired ~~(Pankow et al., 2012; Pankow et al., 1998)~~(Pankow et al., 2012; Pankow et al., 1998). This method is highly complementary to the other instrumentation commonly utilized for NMOC determinations. PTR-MS can measure some polar species not amenable to analysis by GC and in real time, but is limited in the area of compound identification due to the sole reliance on mass-to-charge ratio. In contrast, canister sampling with 1D-GC analysis is ideal for compounds that breakthrough ATD cartridges, but 1D-GC cannot separate a large number of compounds. All of these approaches, in addition to OP-FTIR, were utilized during FLAME-4 ~~(Stockwell et al., 2014) and the measurements will be synthesized in future work~~(Stockwell et al., 2014) and the measurements are being synthesized for publication in a separate manuscript.

The ~~722~~708 compounds positively/tentatively identified across six laboratory burns have afforded unique insights into gas-phase BB emissions. In particular, the identified compounds ~~could~~can be related to the plant composition in a number of ways. The high levels of aromatic hydrocarbons and cyclopentadienes in giant-cutgrass smoke imply high lignin content in this grass species compared to wiregrass, which appears to be more cellulosic in structure based on the high furan emissions. Additionally, the thorough characterization of terpenoids emitted by burning conifer branches ~~allowed~~allow direct correlations to be made between BB emissions and the corresponding essential oils, underscoring that emissions of terpenoid isomers will be specific to individual plant species/fuel types. These measurements have also provided the first comprehensive characterization of intermediate volatility alkanes/alkenes in BB, with compounds up to C$_{15}$ present in most smoke samples and as high as C$_{18}$ in the case of the Indonesian peat fire. Separation of hydrocarbons by double bond equivalents further illustrated a high degree of unsaturation among aliphatic compounds, which will be highly reactive toward atmospheric oxidants. Overall, the distribution of emissions among different compound classes was found to vary considerably from fuel to fuel, indicating that the dominant reaction pathways in aging plumes will be highly dependent on the burned fuel types.

These comprehensive measurements have elucidated a large number of potential SOA precursors in BB emissions, including abundant isomers of aliphatic and aromatic hydrocarbons, phenol derivatives, monoterpenes, and sesquiterpenes. To estimate the relative importance of different precursor classes, the potential SOA mass from each category has been calculated using published SOA yields. Regarding the extent of NMOC oxidation, we have assumed two cases: (1) six hours of oxidation and ~~assuming that~~ representative OH-reactivity for each class, and (2) all precursors react completely (Table 3). ~~For all fuels, aromatic hydrocarbons are predicted~~In comparing cases 1 and 2, it is clear that the phenol, aliphatic HC, terpene, and furan classes react to ~~produce the largest fraction of SOA, ranging from 33% (WG) to 84% (CG). The~~(near) completion after only six hours at [OH] = 2×10^{6} molecules cm^{-3} (Table 3). After six hours, terpenes ~~are also~~emitted from coniferous fuels are expected to contribute significantly to SOA ~~in emissions from coniferous fuels~~ and account for ~~24~~42% and ~~36~~57% of the calculated SOA mass for PP and BS, respectively. SOA produced from aliphatic hydrocarbons was assumed to result from ≥C$_9$ compounds only; the calculated SOA was significant for Indonesian peat BB emissions ~~only~~alone due to the higher molecular weight ~~species~~alkanes/alkenes observed in this sample (Section 3.3.3). In addition to these common SOA precursors, recent research has demonstrated the potential for furans to contribute to SOA formation ~~(Strollo and Ziemann, 2013)~~(Strollo and Ziemann, 2013), indicating that furans may be a previously unconsidered class of SOA precursors in BB smoke. We have assumed 10% SOA yields for all furan derivatives, based on the measured SOA yield of 3-methyl furan ~~(Strollo and Ziemann, 2013)~~(Strollo and Ziemann, 2013). At this SOA yield, furans may produce non-trivial SOA mass, including ~~about one-third~~51% of the SOA calculated from WG emissions after six hours (Table 3). However, because the SOA-formation potential of furfural (the dominant furan derivative in BB) has not been studied, it is unclear if the predicted furan-derived SOA is significantly over or underestimated. At longer oxidation times, SOA derived from aromatic hydrocarbons becomes significant. For all fuels, aromatic hydrocarbons are predicted to produce the largest fraction of SOA, ranging from 31% (WG) to 78% (CG) when all NMOC has reacted (Table 3). Overall, the identified SOA precursors produce estimated OA enhancement ratios on the order of 1.~~02 – 1.2, which is a lower limit based on detected compounds and~~01 – 1.22, depending on the extent of NMOC oxidation. These estimates are in the range of that reported for laboratory experiments ~~(Hennigan et al., 2011; Ortega et al., 2013)~~(Hennigan et al., 2011; Ortega et al., 2013) and ambient BB plumes (Akagi et al., 2012~~; Yokelson et al., 2009)~~; Yokelson et al., 2009)~~.~~, though likely reflect a lower limit based on detected compounds. Because BB dominates global fine POA emissions, even modest enhancements can represent significant production of OA mass.

Despite the range of possible SOA precursors, most atmospheric models treat SOA formation through condensation of surrogates representing the gas-phase oxidation products of a very small number of NMOCs, which typically include benzene, toluene, xylenes, and select biogenic compounds ~~(Odum et al., 1996; Kanakidou et al., 2005; Henze et al., 2008)~~(Carlton et al., 2010; Kanakidou et al., 2005; Odum et al., 1996). Such simplified representations cannot adequately capture the diversity in emissions and plume chemistry that is to be expected based on these GC×GC/TOFMS measurements and other recent efforts ~~(Yokelson et al., 2013)~~(Yokelson et al., 2013). Indeed, recent modeling studies were unable to recreate measured OA levels in BB plumes or BB-influenced regions (Alvarado et al., 2009~~; Heald et al., 2011)~~; Heald et al., 2011), demonstrating that additional precursors and/or formation mechanisms need to be considered. These comprehensive GC×GC/TOFMS emissions measurements provide a significant step in that direction by identifying and quantifying ~~extensive~~a large number of potential SOA precursors. The reported EFs can further supplement ~~the~~ existing BB emission inventories ~~(van der Werf et al., 2010; Wiedinmyer et al., 2011~~(van der Werf et al., 2010; Wiedinmyer et al., 2011; Akagi et al.,

2011) that provide the input for atmospheric BB models~~.~~; the data are available in Table S1. Although computational limits will preclude describing the chemistry of 700+ primary species for the foreseeable future, a subset of the major, ubiquitous species determined herein can serve to focus future modelling efforts.

Acknowledgements

Melissa Roskamp (Portland State University) is thanked for assistance in sampling preparations and testing the ozone scrubbing efficiency of the sodium-thiosulfate impregnated filters. Additional assistance from Lorne Isabelle (Portland State University) is also appreciated. Sonia Kreidenweis and Paul DeMott (Colorado State University) are thanked for helping to coordinate the FLAME-4 campaign. ~~Funding for L.H.~~This work was ~~provided~~supported by a National Science Foundation Atmospheric and Geospace Sciences Postdoctoral Research Fellowship (Grant # 1231128). Additionally, FLAME-4, C. S., and R. Y. were supported by NSF grant ATM-0936321.

References

Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, Environ. Sci. Technol., 42, 4478-4485, Doi 10.1021/Es703009q, 2008.

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmos. Chem. Phys., 11, 4039-4072, DOI 10.5194/acp-11-4039-2011, 2011.

Akagi, S. K., Craven, J. S., Taylor, J. W., McMeeking, G. R., Yokelson, R. J., Burling, I. R., Urbanski, S. P., Wold, C. E., Seinfeld, J. H., Coe, H., Alvarado, M. J., and Weise, D. R.: Evolution of trace gases and particles emitted by a chaparral fire in California, Atmos. Chem. Phys., 12, 1397-1421, 2012.

Akagi, S. K., Yokelson, R. J., Burling, I. R., Meinardi, S., Simpson, I., Blake, D. R., McMeeking, G. R., Sullivan, A., Lee, T., Kreidenweis, S., Urbanski, S., Reardon, J., Griffith, D. W. T., Johnson, T. J., and Weise, D. R.: Measurements of reactive trace gases and variable O-3 formation rates in some South Carolina biomass burning plumes, Atmos. Chem. Phys., 13, 1141-1165, 2013.

Alvarado, A., Atkinson, R., and Arey, J.: Kinetics of the gas-phase reactions of NO3 radicals and O3 with 3-methyl furan and the OH radical yield from the O3 reaction, International Journal of Chemical Kinetics, 28, 905-909, 1996.

Alvarado, M. J., Wang, C., and Prinn, R. G.: Formation of ozone and growth of aerosols in young smoke plumes from biomass burning: 2. Three-dimensional Eulerian studies, J. Geophys. Res. Atmos., 114, Doi 10.1029/2008jd011186, 2009.

~~Alvarado, M. J., Logan, J. A., Mao, J., Apel, E., Riemer, D., Blake, D., Cohen, R. C., Min, K. E., Perring, A. E., Browne, E. C., Wooldridge, P. J., Diskin, G. S., Sachse, G. W., Fuelberg, H., Sessions, W. R., Harrigan, D. L., Huey, G., Liao, J., Case-Hanks, A., Jimenez, J. L., Cubison, M. J., Vay, S. A., Weinheimer, A. J., Knapp, D. J., Montzka, D. D., Flocke, F. M., Pollack, I. B., Wennberg, P. O., Kurten, A., Crounse, J., St Clair, J. M., Wisthaler, A., Mikoviny, T., Yantosca, R. M., Carouge, C. C., and Le Sager, P.: Nitrogen oxides and PAN in plumes from boreal fires during ARCTAS-B and their impact on ozone: an integrated analysis of aircraft and satellite observations, Atmos. Chem. Phys., 10, 9739-9760, 2010.~~

Anderson, A. B., Riffer, R., and Wong, A.: Monoterpenes Fatty and Resin Acids of Pinus Ponderosa and Pinus Jeffreyi, Phytochemistry, 8, 873-&, Doi 10.1016/S0031-9422(00)85876-8, 1969.

Andreae, M. O., and Merlet, P.: Emission of trace gases and aerosols from biomass burning, Global Biogeochem Cy, 15, 955-966, 2001.

Andreae, M. O., Rosenfeld, D., Artaxo, P., Costa, A. A., Frank, G. P., Longo, K. M., and Silva-Dias, M. A. F.: Smoking rain clouds over the Amazon, Science, 303, 1337-1342, Doi 10.1126/Science.1092779, 2004.

Aschmann, S. M., Nishino, N., Arey, J., and Atkinson, R.: Kinetics of the reactions of OH radicals with 2- and 3-methylfuran, 2,3- and 2,5-dimethylfuran, and E- and Z-3-hexene-2,5-dione, and products of OH + 2,5-dimethylfuran, Environ Sci Technol, 45, 1859-1865, 10.1021/es103207k, 2011.

Aschmann, S. M., Nishino, N., Arey, J., and Atkinson, R.: Products of the OH Radical-Initiated Reactions of Furan, 2-and 3-Methylfuran, and 2,3-and 2,5-Dimethylfuran in the Presence of NO, J Phys Chem A, 118, 457-466, 2014.

Atkinson, R., Aschmann, S. M., and Carter, W. P. L.: Kinetics of the reaction of O3 and OH radicals with with Furan and Thiophene at 298 +/- 2K, International Journal of Chemical Kinetics, 15, 51-61, 1983.

Atkinson, R., and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, Atmos. Environ., 37, S197-S219, ~~2003~~2003a.

Atkinson, R., and Arey, J.: Atmospheric Degradation of Volatile Organic Compounds, Chemical Reviews, 103, 4605-4638, 2003b.

Beens, J., Tijssen, R., and Blomberg, J.: Prediction of comprehensive two-dimensional gas chromatographic separations - A theoretical and practical exercise, J Chromatogr A, 822, 233-251, 1998.

Bierbach, A., Barnes, I., and Becker, K. H.: Rate coefficients for the gas-phase reactions of hydroxyl radicals with furan, 2-methylfuran, 2-ethylfuran, and 2,5-dimethylfuran, Atmos. Environ., 26A, 813-817, 1992.

Bierbach, A., Barnes, I., and Becker, K. H.: Product and kinetic study of the OH-initiated gas-phase oxidation of furan, 2-methylfuran, and furanaldehydes at 300K, Atmos. Environ., 29, 2651-2660, 1995.

Bouvier-Brown, N. C., Goldstein, A. H., Gilman, J. B., Kuster, W. C., and de Gouw, J. A.: In-situ ambient quantification of monoterpenes, sesquiterpenes, and related oxygenated compounds during BEARPEX 2007: implications for gas- and particle-phase chemistry, Atmos. Chem. Phys., 9, 5505-5518, 2009.

Brockway, D. G., and Lewis, C. E.: Long-term effects of dormant-season prescribed fire on plant community diversity, structure and productivity in a longleaf pine wiregrass ecosystem, Forest Ecol Manag, 96, 167-183, 1997.

Cabañas, B., Baeza, M. T., MartÍn, P., Salgado, S., Villanueva, F., Monedero, E., and Wirtz, K.: Products and Mechanism of the NO3 Reaction with Thiophene, J. Atmos. Chem., 51, 317-335, 10.1007/s10874-005-3580-5, 2005.

Carlton, A. G., Bhave, P. V., Napelenok, S. L., Edney, E. D., Sarwar, G., Pinder, R. W., Pouliot, G. A., and Houyoux, M.: Model Representation of Secondary Organic Aerosol in CMAQv4.7, Environ. Sci. Technol., 44, 8553-8560, 10.1021/es100636q, 2010.

Chan, A. W. H., Chan, M. N., Surratt, J. D., Chhabra, P. S., Loza, C. L., Crounse, J. D., Yee, L. D., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Role of aldehyde chemistry and NOx concentrations in secondary organic aerosol formation, Atmos. Chem. Phys., 10, 7169-7188, 2010.

Chan, K. M., Huang, D. D., Li, Y. J., Chan, M. N., Seinfeld, J. H., and Chan, C. K.: Oligomeric products and formation mechanisms from acid-catalyzed reactions of methyl vinyl ketone on acidic sulfate particles, J. Atmos. Chem., 70, 1-18, Doi 10.1007/S10874-013-9248-7, 2013.

Chan, M. N., Kautzman, K. E., Chhabra, P. S., Surratt, J. D., Chan, M. N., Crounse, J. D., Kurten, A., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from photooxidation of naphthalene and alkylnapthalenes: implications for oxidation of intermediate volatility organic compounds (IVOCs), Atmos. Chem. Phys., 9, 3049-3060, 2009.

Chang, D., and Song, Y.: Estimates of biomass burning emissions in tropical Asia based on satellite-derived data, Atmos. Chem. Phys., 10, 2335-2351, 2010.

Christian, T. J., Kleiss, B., Yokelson, R. J., Holzinger, R., Crutzen, P. J., Hao, W. M., Saharjo, B. H., and Ward, D. E.: Comprehensive laboratory measurements of biomass-burning emissions: 1. Emissions from Indonesian, African, and other fuels, J. Geophys. Res. Atmos., 108, Doi 10.1029/2003jd003704, 2003.

Christian, T. J., Kleiss, B., Yokelson, R. J., Holzinger, R., Crutzen, P. J., Hao, W. M., Shirai, T., and Blake, D. R.: Comprehensive laboratory measurements of biomass-burning emissions: 2. First intercomparison of open-path FTIR, PTR-MS, and GC- MS/FID/ECD, J. Geophys. Res. Atmos., 109, Doi 10.1029/2003jd003874, 2004.

Ciccioli, P., Brancaleoni, E., Frattoni, M., Cecinato, A., and Pinciarelli, L.: Determination of volatile organic compounds (VOC) emitted from biomass burning of Mediterranean vegetation species by GC-MS, Anal Lett, 34, 937-955, 2001.

Colmenar, I., Cabañas, B., Martínez, E., Salgado, M. S., and Martín, P.: Atmospheric fate of a series of furanaldehydes by their NO3 reactions, Atmos. Environ., 54, 177-184, 10.1016/j.atmosenv.2012.02.087, 2012.

Crutzen, P. J., and Andreae, M. O.: Biomass Burning in the Tropics - Impact on Atmospheric Chemistry and Biogeochemical Cycles, Science, 250, 1669-1678, 1990.

Cumming, S. G.: Forest type and wildfire in the alberta boreal mixedwood: What do fires burn?, Ecol Appl, 11, 97-110, 2001.

Desalmand, F., and Serpolay, R.: Some specific features of the aerosol-particle concentrations during the dry season and during a bushfire event in West-Africa, Atmos. Environ., 19, 1535-1543, 1985.

Eom, I. Y., Kim, J. Y., Kim, T. S., Lee, S. M., Choi, D., Choi, I. G., and Choi, J. W.: Effect of essential inorganic metals on primary thermal degradation of lignocellulosic biomass, Bioresource Technol, 104, 687-694, 10.1016/j.biortech.2011.10.035, 2012.

Eom, I. Y., Kim, J. Y., Lee, S. M., Cho, T. S., Yeo, H., and Choi, J. W.: Comparison of pyrolytic products produced from inorganic-rich and demineralized rice straw (Oryza sativa L.) by fluidized bed pyrolyzer for future biorefinery approach, Bioresource Technol, 128, 664-672, Doi 10.1016/J.Biortech.2012.09.082, 2013.

Finlayson-Pitts, B. J., and Pitts, J. N.: Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications, Academic Press, San Diego, 2000.

Fitzpatrick, E. M., Jones, J. A., Pourkashanian, M., Ross, A. B., Williams, A., and Bartle, K. D.: Mechanistic aspects of soot formation from the combustion of pine wood, Energy Fuels, 22, 3771-3778, 2008.

Friedli, H. R., Atlas, E., Stroud, V. R., Giovanni, L., Campos, T., and Radke, L. F.: Volatile organic trace gases emitted from North American wildfires, Global Biogeochem Cy, 15, 435-452, 2001.

Gómez Alvarez, E., Borrás, E., Viidanoja, J., and Hjorth, J.: Unsaturated dicarbonyl products from the OH-initiated photo-oxidation of furan, 2-methylfuran and 3-methylfuran, Atmos. Environ., 43, 1603-1612, 10.1016/j.atmosenv.2008.12.019, 2009.

Goode, J. G., Yokelson, R. J., Ward, D. E., Susott, R. A., Babbitt, R. E., Davies, M. A., and Hao, W. M.: Measurements of excess O-3, CO2, CO, CH4, C2H4, C2H2, HCN, NO, NH3, HCOOH, CH3COOH, HCHO, and CH3OH in 1997 Alaskan biomass burning plumes by airborne fourier transform infrared spectroscopy (AFTIR), J. Geophys. Res. Atmos., 105, 22147-22166, 2000.

Grieshop, A. P., Logue, J. M., Donahue, N. M., and Robinson, A. L.: Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 1: measurement and simulation of organic aerosol evolution, Atmos. Chem. Phys., 9, 1263-1277, 2009.

Griffin, R. J., Cocker, D. R., Flagan, R. C., and Seinfeld, J. H.: Organic aerosol formation from the oxidation of biogenic hydrocarbons, J. Geophys. Res., 104, 3555-3567, 1999.

Haines, T. K., and Busby, R. L.: Prescribed burning in the South: Trends, purpose, and barriers, Journal of Applied Forestry, 25, 149-153, 2001.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155-5236, 2009.

Hatfield, M. L., and Hartz, K. E. H.: Secondary organic aerosol from biogenic volatile organic compound mixtures, Atmos. Environ., 45, 2211-2219, 2011.

Heald, C. L., Coe, H., Jimenez, J. L., Weber, R. J., Bahreini, R., Middlebrook, A. M., Russell, L. M., Jolleys, M., Fu, T. M., Allan, J. D., Bower, K. N., Capes, G., Crosier, J., Morgan, W. T., Robinson, N. H., Williams, P. I., Cubison, M. J., DeCarlo, P. F., and Dunlea, E. J.: Exploring the vertical profile of atmospheric organic aerosol: comparing 17 aircraft field campaigns with a global model, Atmos. Chem. Phys., 11, 12673-12696, Doi 10.5194/Acp-11-12673-2011, 2011.

Heil, A.: Indonesian forest and peat fires: Emissions, air quality, and human health, Ph.D., Max Planck Institute for Meteorology, Hamburg, 142 pp., 2007.

Helmig, D.: Ozone removal techniques in the sampling of atmospheric volatile organic trace gases, Atmos. Environ., 31, 3635-3651, 1997.

Helmig, D., Revermann, T., Pollmann, J., Kaltschmidt, O., Hernandez, A. J., Bocquet, F., and David, D.: Calibration system and analytical considerations for quantitative sesquiterpene measurements in air, J Chromatogr A, 1002, 193-211, 10.1016/s0021-9673(03)00619-8, 2003.

Helmig, D., Bocquet, F., Pollmann, J., and Revermann, T.: Analytical techniques for sesquiterpene emission rate studies in vegetation enclosure experiments, Atmos. Environ., 38, 557-572, 10.1016/j.atmosenv.2003.10.012, 2004.

Hennigan, C. J., Miracolo, M. A., Engelhart, G. J., May, A. A., Presto, A. A., Lee, T., Sullivan, A. P., McMeeking, G. R., Coe, H., Wold, C. E., Hao, W. M., Gilman, J. B., Kuster, W. C., de Gouw, J., Schichtel, B. A., Collett, J. L., Kreidenweis, S. M., and Robinson, A. L.:

Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber, Atmos. Chem. Phys., 11, 7669-7686, DOI 10.5194/acp-11-7669-2011, 2011.

~~Henze, D. K., Seinfeld, J. H., Ng, N. L., Kroll, J. H., Fu, T. M., Jacob, D. J., and Heald, C. L.: Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: high- vs. low-yield pathways, Atmos. Chem. Phys., 8, 2405-2420, 2008.~~

Hobbs, P. V., Reid, J. S., Kotchenruther, R. A., Ferek, R. J., and Weiss, R.: Direct radiative forcing by smoke from biomass burning, Science, 275, 1776-1778, 1997.

Hobbs, P. V., Sinha, P., Yokelson, R. J., Christian, T. J., Blake, D. R., Gao, S., Kirchstetter, T. W., Novakov, T., and Pilewskie, P.: Evolution of gases and particles from a savanna fire in South Africa, J. Geophys. Res. Atmos., 108, Artn 8485

Doi 10.1029/2002jd002352, 2003.

Jaffe, D., Bertschi, I., Jaegle, L., Novelli, P., Reid, J. S., Tanimoto, H., Vingarzan, R., and Westphal, D. L.: Long-range transport of Siberian biomass burning emissions and impact on surface ozone in western North America, Geophys. Res. Lett., 31, Artn L16106

Doi 10.1029/2004gl020093, 2004.

Jiang, G. Z., Nowakowski, D. J., and Bridgwater, A. V.: Effect of the Temperature on the Composition of Lignin Pyrolysis Products, Energy Fuels, 24, 4470-4475, 2010.

Jolleys, M. D., Coe, H., McFiggans, G., Capes, G., Allan, J. D., Crosier, J., Williams, P. I., Allen, G., Bower, K. N., Jimenez, J. L., Russell, L. M., Grutter, M., and Baumgardner, D.: Characterizing the aging of biomass burning organic aerosol by use of mixing ratios: A meta-analysis of four regions, Environ. Sci. Technol., 46, 13093-13102, 2012.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053-1123, 2005.

Kesselmeier, J., and Staudt, M.: Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology, J. Atmos. Chem., 33, 23-88, 1999.

Krauze-Baranowska, M., Mardarowicz, M., Wiwart, M., Poblocka, L., and Dynowska, M.: Antifungal activity of the essential oils from some species of the genus Pinus, Z Naturforsch C, 57, 478-482, 2002.

Kroll, J. H., and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, Atmos. Environ., 42, 3593-3624, DOI 10.1016/j.atmosenv.2008.01.003, 2008.

Laskin, A., Smith, J. S., and Laskin, J.: Molecular characterization of nitrogen-containing organic compounds in biomass burning aerosols using high-resolution mass spectrometry, Environ. Sci. Technol., 43, 3764-3771, 2009.

Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, J. Geophys. Res., 111, 10.1029/2006jd007050, 2006.

Lim, Y. B., and Ziemann, P. J.: Effects of molecular structure on aerosol yields from OH radical-initiated reactions of linear, branched, and cyclic alkanes in the presence of NOx, Environ. Sci. Technol., 43, 2328-2334, Doi 10.1021/Es803389s, 2009.

Linstrom, P. J., and Mallard, W. G., Eds., National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov, 2014.

Liu, Y., Siekmann, F., Renard, P., El Zein, A., Salque, G., El Haddad, I., Temime-Roussel, B., Voisin, D., Thissen, R., and Monod, A.: Oligomer and SOA formation through aqueous phase photooxidation of methacrolein and methyl vinyl ketone, Atmos. Environ., 49, 123-129, Doi 10.1016/J.Atmosenv.2011.12.012, 2012.

Lobert, J. M., and Warnatz, J.: Emissions from the Combustion Process in Vegetation, in: Fire in the Environment: The Ecological, Atmospheric, and Climatic Importance of Vegetation Fires, edited by: Crutzen, P. J., and Goldammer, J. G., John Wiley & Sons Ltd., New York, 15-37, 1993.

Lohmann, U., and Feichter, J.: Global indirect aerosol effects: a review, Atmos. Chem. Phys., 5, 715-737, 2005.

Ma, Y., Hays, M. D., Geron, C. D., Walker, J. T., and Gichuru, M. J. G.: Technical Note: Fast two-dimensional GC-MS with thermal extraction for anhydro-sugars in fine aerosols, Atmos. Chem. Phys., 10, 4331-4341, DOI 10.5194/acp-10-4331-2010, 2010.

Ma, Y. L., and Hays, M. D.: Thermal extraction-two-dimensional gas chromatography-mass spectrometry with heart-cutting for nitrogen heterocyclics in biomass burning aerosols, J Chromatogr A, 1200, 228-234, DOI 10.1016/j.chroma.2008.05.078, 2008.

Matsunaga, A., Docherty, K. S., Lim, Y. B., and Ziemann, P. J.: Composition and yields of secondary organic aerosol formed from OH radical-initiated reactions of linear alkenes in the presence of NOx: Modeling and measurements, Atmos. Environ., 43, 1349-1357, 2009.

McMeeking, G. R., Kreidenweis, S. M., Baker, S., Carrico, C. M., Chow, J. C., Collett, J. L., Hao, W. M., Holden, A. S., Kirchstetter, T. W., Malm, W. C., Moosmuller, H., Sullivan, A. P., and Wold, C. E.: Emissions of trace gases and aerosols during the open combustion of biomass in the laboratory, J. Geophys. Res. Atmos., 114, Doi 10.1029/2009jd011836, 2009.

Meinardi, S., Simpson, I. J., Blake, N. J., Blake, D. R., and Rowland, F. S.: Dimethyl disulfide (DMDS) and dimethyl sulfide (DMS) emissions from biomass burning in Australia, Geophys. Res. Lett., 30, 2003.

Mondello, L., Tranchida, P. Q., Dugo, P., and Dugo, G.: Comprehensive two-dimensional gas chromatography-mass spectrometry: A review, Mass Spectrom Rev, 27, 101-124, Doi 10.1002/Mas.20158, 2008.

Mulholland, J. A., Lu, M., and Kim, D. H.: Pyrolytic growth of polycyclic aromatic hydrocarbons by cyclopentadienyl moieties, P Combust Inst, 28, 2593-2599, 2000.

Nakao, S., Clark, C., Tang, P., Sato, K., and Cocker, D.: Secondary organic aerosol formation from phenolic compounds in the absence of NOx, Atmos. Chem. Phys., 11, 10649-10660, 2011.

Nara, H., Nakagawa, F., and Yoshida, N.: Development of two-dimensional gas chromatography/isotope ratio mass spectrometry for the stable carbon isotopic analysis Of C(2)-C(5) non-methane hydrocarbons emitted from biomass burning, Rapid Commun Mass Sp, 20, 241-247, Doi 10.1002/Rcm.2302, 2006.

Nasri, N., Tlili, N., Triki, S., Elfalleh, W., Cheraif, I., and Khaldi, A.: Volatile Constituents of Pinus pinea L. Needles, J Essent Oil Res, 23, 15-19, 2011.

Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, Atmos. Chem. Phys., 7, 3909-3922, 2007.

Oanh, N. T. K., Ly, B. T., Tipayarom, D., Manandhar, B. R., Prapat, P., Simpson, C. D., and Liu, L. J. S.: Characterization of particulate matter emission from open burning of rice straw, Atmos. Environ., 45, 493-502, Doi 10.1016/J.Atmosenv.2010.09.023, 2011.

Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C., and Seinfeld, J. H.: Gas/particle partitioning and secondary organic aerosol yields, Environ. Sci. Technol., 30, 2580-2585, Doi 10.1021/Es950943+, 1996.

Ortega, A. M., Day, D. A., Cubison, M. J., Brune, W. H., Bon, D., de Gouw, J. A., and Jimenez, J. L.: Secondary organic aerosol formation and primary organic aerosol oxidation from biomass-burning smoke in a flow reactor during FLAME-3, Atmos. Chem. Phys., 13, 11551-11571, 2013.

Page, S. E., Siegert, F., Rieley, J. O., Boehm, H. D. V., Jaya, A., and Limin, S.: The amount of carbon released from peat and forest fires in Indonesia during 1997, Nature, 420, 61-65, 2002.

Paine, J. B., Pithawalla, Y. B., and Naworal, J. D.: Carbohydrate pyrolysis mechanisms from isotopic labeling~~. Part 3. The Pyrolysis of D-glucose: Formation of C-3 and C-4 carbonyl compounds and a cyclopentenedione isomer by electrocyclic fragmentation mechanisms, J Anal Appl Pyrol, 82, 42-69, 2008a.~~

~~Paine, J. B., Pithawalla, Y. B., and Naworal, J. D.: Carbohydrate pyrolysis mechanisms from isotopic labeling Part 4.~~ Part 4. The pyrolysis Of D-glucose: The formation of furans, J Anal Appl Pyrol, 83, 37-63, ~~2008b~~2008a.

Paine, J. B., Pithawalla, Y. B., and Naworal, J. D.: Carbohydrate pyrolysis mechanisms from isotopic labeling. Part 3. The Pyrolysis of D-glucose: Formation of C-3 and C-4 carbonyl compounds and a cyclopentenedione isomer by electrocyclic fragmentation mechanisms, J Anal Appl Pyrol, 82, 42-69, 2008b.

Pandey, M. P., and Kim, C. S.: Lignin Depolymerization and Conversion: A Review of Thermochemical Methods, Chem. Eng. Technol., 34, 29-41, 10.1002/ceat.201000270, 2011.

Pankow, J. F., Luo, W. T., Isabelle, L. M., Bender, D. A., and Baker, R. J.: Determination of a wide range of volatile organic compounds in ambient air using multisorbent adsorption/thermal desorption and gas chromatography mass spectrometry, Anal Chem, 70, 5213-5221, Doi 10.1021/Ac980481t, 1998.

Pankow, J. F., Luo, W., Melnychenko, A. N., Barsanti, K. C., Isabelle, L. M., Chen, C., Guenther, A. B., and Rosenstiel, T. N.: Volatilizable Biogenic Organic Compounds (VBOCs) with two dimensional Gas Chromatography-Time of Flight Mass Spectrometry (GC x GC-TOFMS): sampling methods, VBOC complexity, and chromatographic retention data, Atmos. Meas. Tech., 5, 345-361, Doi 10.5194/Amt-5-345-2012, 2012.

Patwardhan, P. R., Satrio, J. A., Brown, R. C., and Shanks, B. H.: Influence of inorganic salts on the primary pyrolysis products of cellulose, Bioresource Technol, 101, 4646-4655, Doi 10.1016/J.Biortech.2010.01.112, 2010.

Petters, M. D., Parsons, M. T., Prenni, A. J., DeMott, P. J., Kreidenweis, S. M., Carrico, C. M., Sullivan, A. P., McMeeking, G. R., Levin, E., Wold, C. E., Collett, J. L., and Moosmuller, H.: Ice nuclei emissions from biomass burning, J. Geophys. Res. Atmos., 114, Doi 10.1029/2008jd011532, 2009.

Pollmann, J., Ortega, J., and Helmig, D.: Analysis of atmospheric sesquiterpenes: Sampling losses and mitigation of ozone interferences, Environ. Sci. Technol., 39, 9620-9629, 2005.

~~Poschl, U.: Atmospheric aerosols: Composition, transformation, climate and health effects, Angew Chem Int Edit, 44, 7520-7540, DOI 10.1002/anie.200501122, 2005.~~

Pope, C. A., and Dockery, D. W.: Health effects of fine particulate air pollution: Lines that connect, J Air Waste Manage, 56, 709-742, 2006.

Presto, A. A., Miracolo, M. A., Donahue, N. M., and Robinson, A. L.: Secondary organic aerosol formation from high-NOx photo-oxidation of low volatility precursors: n-Alkanes, Environ. Sci. Technol., 44, 2029-2034, 2010.

Reid, J. S., Koppmann, R., Eck, T. F., and Eleuterio, D. P.: A review of biomass burning emissions part II: intensive physical properties of biomass burning particles, Atmos. Chem. Phys., 5, 799-825, 2005.

Saiz-Jimenez, C., and De Leeuw, J. W.: Lignin pyrolysis products: Their structures and their significance as biomarkers Organic Geochemistry, 10, 869-876, 1986.

Saxena, P., Hildemann, L. M., Mcmurry, P. H., and Seinfeld, J. H.: Organics alter hygroscopic behavior of atmospheric particles, J. Geophys. Res. Atmos., 100, 18755-18770, 1995.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources. 3. C-1-C-29 organic compounds from fireplace combustion of wood, Environ. Sci. Technol., 35, 1716-1728, 2001.

Seinfeld, J. H., and Pankow, J. F.: Organic atmospheric particulate material, Annu Rev Phys Chem, 54, 121-140, DOI 10.1146/annurev.physchem.54.011002.103756, 2003.

Shafizadeh, F.: Introduction to Pyrolysis of Biomass, J Anal Appl Pyrol, 3, 283-305, 1982.

Simpson, I. J., Akagi, S. K., Barletta, B., Blake, N. J., Choi, Y., Diskin, G. S., Fried, A., Fuelberg, H. E., Meinardi, S., Rowland, F. S., Vay, S. A., Weinheimer, A. J., Wennberg, P. O., Wiebring, P., Wisthaler, A., Yang, M., Yokelson, R. J., and Blake, D. R.: Boreal forest fire emissions in fresh Canadian smoke plumes: C(1)-C(10) volatile organic compounds (VOCs), CO(2), CO, NO(2), NO, HCN and CH(3)CN, Atmos. Chem. Phys., 11, 6445-6463, DOI 10.5194/acp-11-6445-2011, 2011.

Smith, J. D., Sio, V., Yu, L., Zhang, Q., and Anastasio, C.: Secondary organic aerosol production from aqueous reactions of atmospheric phenols with an organic triplet excited state, Environ. Sci. Technol., 48, 1049-1057, Doi 10.1021/Es4045715, 2014.

Sojak, L., Hrivnak, J., Majer, P., and Janak, J.: Capillary gas-chromatography of linear alkenes on squalane, Anal Chem, 45, 293-302, 1973.

Sojak, L., Kralovicova, E., Ostrovsky, I., and Leclercq, P. A.: Retention behavior of conjugated and isolated normal-alkadienes - identification of normal-nonadiene and normal-decadiene by capillary gas-chromatography using structure retention correlations and mass-spectrometry, J Chromatogr, 292, 241-261, 1984.

Stein, S. E.: Retention Indices, in: NIST Chemistry WebBook, NIST Standard Reference Database Number 69, edited by: Linstrom, P. J., and Mallard, W. G., National Institute of Standards and Technology, Gaithersburg, MD, 2013.

Stockwell, C. E., Yokelson, R. J., Kreidenweis, S. M., Robinson, A. L., DeMott, P. J., Sullivan, R. C., Reardon, J., Ryan, K. C., Griffith, D. W. T., and Stevens, L.: Trace gas emissions from combustion of peat, crop residue, biofuels, grasses, and other fuels: configuration and FTIR component of the fourth Fire Lab at Missoula Experiment (FLAME-4), Atmos. Chem. Phys~~. Discuss~~., 14, ~~10061-10134~~9727-9754, 2014.

Stolle, A., Ondruschka, B., and Hopf, H.: Thermal Rearrangements of Monoterpenes and Monoterpenoids, Helvetica Chimica Acta, 92, 1673-1719, 2009.

Streets, D. G., Yarber, K. F., Woo, J. H., and Carmichael, G. R.: Biomass burning in Asia: Annual and seasonal estimates and atmospheric emissions, Global Biogeochem Cy, 17, 10.1029/2003GB002040, 2003.

Strollo, C. M., and Ziemann, P. J.: Products and mechanism of secondary organic aerosol formation from the reaction of 3-methylfuran with OH radicals in the presence of NOx, Atmos. Environ., 77, 534-543, 2013.

Sun, Y. L., Zhang, Q., Anastasio, C., and Sun, J.: Insights into secondary organic aerosol formed via aqueous-phase reactions of phenolic compounds based on high resolution mass spectrometry, Atmos. Chem. Phys., 10, 4809-4822, 10.5194/acp-10-4809-2010, 2010.

Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, J Phys Chem A, 110, 9665-9690, 2006.

Tong, H. Y., and Karasek, F. W.: Flame ionization detector response factors for compound classes in quantitative-analysis of complex organic mixtures, Anal Chem, 56, 2124-2128, 1984.

USDA, N., The PLANTS Database (http://plants.usda.gov), National Plant Data Team, Greensboro, NC 27401-4901 USA, 2014.

Vakkari, V., Kerminen, V. M., Beukes, J. P., Tiitta, P., van Zyl, P. G., Josipovic, M., Venter, A. D., Jaars, K., Worsnop, D. R., Kulmala, M., and Laakso, L.: Rapid changes in biomass burning aerosols by atmospheric oxidation, Geophys. Res. Lett., 41, 2644-2651, 10.1002/2014gl059396, 2014.

van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., Morton, D. C., DeFries, R. S., Jin, Y., and van Leeuwen, T. T.: Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997-2009), Atmos. Chem. Phys., 10, 11707-11735, 10.5194/acp-10-11707-2010, 2010.

Veblen, T. T., Kitzberger, T., and Donnegan, J.: Climatic and human influences on fire regimes in ponderosa pine forests in the Colorado Front Range, Ecol Appl, 10, 1178-1195, 2000.

von Rudloff, E.: Seasonal Variation in the Terpenes of the Foliage of Black Spruce, Phytochemistry, 14, 1695-1699, 1975.

Wade, D. D., Brock, B. L., Brose, P. H., Grace, J. B., Hoch, G. A., and Patterson, W. A.: Fire in Eastern Ecosystems, ~~USDA~~in: Wildland Fire in Ecosystems: Effects of Fire on Flora. Gen. Tech. Rep. RMRS-GTR-42-vol. 2, edited by: Brown, J. K., and Smith, J. K., U.S. Department of Agriculture, Forest Service ~~General Technical Report RMRS-GTR-42~~, Rocky Mountain Research Station, Ogden, UT, 53-96, 2000.

~~Wang, Q., Jacob, D. J., Fisher, J. A., Mao, J., Leibensperger, E. M., Carouge, C. C., Le Sager, P., Kondo, Y., Jimenez, J. L., Cubison, M. J., and Doherty, S. J.: Sources of carbonaceous aerosols and deposited black carbon in the Arctic in winter-spring: implications for radiative forcing, Atmos. Chem. Phys., 11, 12453-12473, Doi 10.5194/Acp-11-12453-2011, 2011.~~

Ward, D. E.: Factors Influencing the Emissions of Gases and Particulate Matter from Biomass Burning, in: Fire in the Tropical Biota: Ecosystem Processes and Global Challenges, edited by: Goldammer, J. G., Springer-Verlag, Berlin, Germany, 418-436, 1990.

Warneke, C., Roberts, J. M., Veres, P., Gilman, J., Kuster, W. C., Burling, I., Yokelson, R., and de Gouw, J. A.: VOC identification and inter-comparison from laboratory biomass burning using PTR-MS and PIT-MS, Int. J. Mass. Spectrom., 303, 6-14, DOI 10.1016/j.ijms.2010.12.002, 2011.

Wiedinmyer, C., Akagi, S. K., Yokelson, R. J., Emmons, L. K., Al-Saadi, J. A., Orlando, J. J., and Soja, A. J.: The Fire INventory from NCAR (FINN): a high resolution global model to estimate the emissions from open burning, Geosci Model Dev, 4, 625-641, DOI 10.5194/gmd-4-625-2011, 2011.

Wigder, N. L., Jaffe, D. A., and Saketa, F. A.: Ozone and particulate matter enhancements from regional wildfires observed at Mount Bachelor during 2004-2011, Atmos. Environ., 75, 24-31, 2013.

Yee, L. D., Kautzman, K. E., Loza, C. L., Schilling, K. A., Coggon, M. M., Chhabra, P. S., Chan, M. N., Chan, A. W. H., Hersey, S. P., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from biomass burning intermediates: phenol and methoxyphenols, Atmos. Chem. Phys., 13, 8019-8043, 2013.

Yokelson, R. J., Griffith, D. W. T., and Ward, D. E.: Open-path Fourier transform infrared studies of large-scale laboratory biomass fires, J. Geophys. Res. Atmos., 101, 21067-21080, 1996.

Yokelson, R. J., Goode, J. G., Ward, D. E., Susott, R. A., Babbitt, R. E., Wade, D. D., Bertschi, I., Griffith, D. W. T., and Hao, W. M.: Emissions of formaldehyde, acetic acid, methanol, and other trace gases from biomass fires in North Carolina measured by airborne Fourier transform infrared spectroscopy, J. Geophys. Res., 104, 30,109-130,125, 1999.

Yokelson, R. J., Bertschi, I. T., Christian, T. J., Hobbs, P. V., Ward, D. E., and Hao, W. M.: Trace gas measurements in nascent, aged, and cloud-processed smoke from African savanna fires by airborne Fourier transform infrared spectroscopy (AFTIR), J. Geophys. Res. Atmos., 108, Doi 10.1029/2002jd002322, 2003.

Yokelson, R. J., Crounse, J. D., DeCarlo, P. F., Karl, T., Urbanski, S., Atlas, E., Campos, T., Shinozuka, Y., Kapustin, V., Clarke, A. D., Weinheimer, A., Knapp, D. J., Montzka, D. D., Holloway, J., Weibring, P., Flocke, F., Zheng, W., Toohey, D., Wennberg, P. O., Wiedinmyer, C., Mauldin, L., Fried, A., Richter, D., Walega, J., Jimenez, J. L., Adachi, K., Buseck, P. R., Hall, S. R., and Shetter, R.: Emissions from biomass burning in the Yucatan, Atmos. Chem. Phys., 9, 5785-5812, 2009.

Yokelson, R. J., Burling, I. R., Gilman, J. B., Warneke, C., Stockwell, C. E., de Gouw, J., Akagi, S. K., Urbanski, S. P., Veres, P., Roberts, J. M., Kuster, W. C., Reardon, J., Griffith, D. W. T., Johnson, T. J., Hosseini, S., Miller, J. W., Cocker, D. R., Jung, H., and Weise, D.

R.: Coupling field and laboratory measurements to estimate the emission factors of identified and unidentified trace gases for prescribed fires, Atmos. Chem. Phys., 13, 89-116, 2013.

Ziemann, P. J.: Effects of molecular structure on the chemistry of aerosol formation from the OH-radical-initiated oxidation of alkanes and alkenes, Int Rev Phys Chem, 30, 161-195, 2011.

Ziemann, P. J., and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol formation, Chemical Society reviews, 41, 6582-6605, 2012.