Responses to Referee Comments for ACP 2019

Referee #2

Referee Comments: This is interesting work attempting to identify and quantify emissions specifically from the "pyrolysis process" preceding combustion from a prescribed fire. Trace gases were sampled using canisters and quantified offline by FTIR. Emission ratios and emission factors were calculated and compared to a few previous publications. The authors use Sekimoto et al. 2018's ratio of ethyne to furan along with reporting higher ERs for several species compared to other studies as evidence that there was selective sampling of high-temperature pyrolysis emissions. Altogether, this is insufficient evidence that pyrolysis only emissions were selectively captured by the custom sampling device. It is unclear how this body of work is useful to modelers as pyrolysis products are only part of the total fire emissions necessary to accurately model fire. While it does little to inform us about best practices for prescribed burn conditions, it is an interesting attempt to isolate pyrolysis compounds in an "uncontrolled" real-world setting, however, there are entire journals (e.g. Journal of Analytical and Applied Pyrolysis, Fuel, etc.) dedicated to identifying the chemical products from pyrolysis. There is insufficient motivation for why this data is useful and the authors have not made a strong case for publication. It is likely these partial fire results have a strong potential to mislead or confuse the casual reader.

***Author Comments:** We thank the referee for the comment, but respectfully disagree with certain aspects of the comment. Along with the first referee and the editor, we believe that this paper represents one of the first, if not the seminal paper, to report field measurements of largely pyrolysis emissions. The referee is correct that there are many other studies of pyrolysis in other journals, but nearly all those studies are controlled laboratory experiments, often in oxygen-free environments utilizing ground (powdered) fuel samples in order to minimize heat transfer effects. This paper is devoted to much more challenging field experiments and should be published as such. It is part of a larger pyrolysis study wherein pyrolysis products from the same plant species are being measured in 1) oxygen-free environment using intact foliage samples, 2) in an atmospheric oxygen wind tunnel setting with relatively simple heterogeneous fuel beds, and 3) in small field burns. One of the goals of the larger study is to determine the relationship between the controlled lab results and actual fire conditions in the field for pyrolysis as was done previously by Yokelson et al. (2013) largely for the combustion and smoldering phases. Results from our objectives 1) and 2) have been published in the open journals and further context to put the present manuscript in perspective have been added. The referee's comment that the gases sampled via our method are not strictly pyrolysis gases is entirely correct. We have mentioned repeatedly in the text that our methods were an imperfect set of "molecular tweezers" to try to capture those pyrolysis species. As discussed in the paper, we believe that we are capturing a much larger fraction of pyrolysis and early-phase species as compared to capturing post-combustion emissions.

Referee Comments: In the introduction, a lot of emphasis is placed on the importance of identifying and quantifying biomass burning emissions for model predictions, which guide best practices for prescribed burning conditions. Additionally, the authors highlight the complexities of fires and emission dependencies on fuel types, burn techniques, geometry, etc., however, there isn't proper support/justification for why measurements of just the pyrolysis emissions is vital for these sorts of model predictions or for analyzing burn techniques. A more "realistic" set of emission factors is obtained following combustion as many of the products measured during "pyrolysis only" will likely be consumed and/or combusted in the flame at higher temperatures resulting in different chemical products.

***Author Comments:** The referee is correct that smoke composition values for smoke gathered after the onset of combustion are the more useful data for downwind atmospheric models. The focus of the present work, however, is to provide understanding as well as data for physics-based models of the combustion and fire spread process. These models, such as FIRETEC and FDS, often model the process of pyrolysis based on results for wood or on ground foliage samples. An improved modeling of pyrolysis in these models provides an improved suite of chemical species which are then combusted in the models to estimate heat release rates and products of combustion. The focus of the present paper is to better understand the chemistry and physics of the very early stages of the burning process, knowledge which can in an indirect way contribute to realistic chemical models. Still, we have modified the text accordingly so as not to mislead the reader that early stage fire product studies will contribute directly to those models.

Referee Comments: The introduction is quite long and needs to remain more focused. It covers everything including downwind formation measured by FTIR to a significant discussion of MCE. It may be useful to rearrange and focus the introduction on motivation and important background considerations of FTIR sampling and pyrolysis measurements and move MCE discussions later in the manuscript.

***Author Comments:** We thank the referee for this comment; we have taken this suggestion to heart. The MCE section was moved to the discussion and the entire introduction has been substantially revised.

Referee Comments: P4 L 80 There is some discussion in the introduction about the importance of prescribed burning and here the authors reference the necessity to understand burn conditions to minimize gases released during prescribed burns. It may be persuasive to highlight Liu et al., 2017, which provides clear evidence that the PM emitted from a wildfire is much greater than that for a controlled prescribed burn. While the authors have steered clear of PM discussion, this still highlights some major differences observed between the two. It may also be useful to highlight some of the differences between a prescribed burn versus a wildfire in terms of fuel consumption as well as considerations on meteorological and fuel moisture conditions. Liu, X., et al. (2017), Airborne measurements of western U.S. wildfire emissions: Comparison with prescribed burning and air quality implications, J. Geophys. Res. Atmos., 122, 6108– 6129, doi:10.1002/2016JD026315

***Author Comments:** We thank the referee for their comments, and his/her knowledge of the literature. We have modified the text to directly reflect these comments and added the citations.

Referee Comments: P4 L 89 It is incorrectly stated that pyrolysis is the "first step" in the burning process. Initially there is evaporation of water and other gases absorbed to the solid fuel (distillation), then once the temperature gets high enough to break bonds in the solid fuel both organic aerosol and non-methane organic gases are given off (pyrolysis) and this flammable mixture serves as the airborne fuel that can be rapidly oxidized. Some of the pyrolysis products are processed in the flame to CO_2 and BC, however, much of it escapes unoxidized. Entrainments of unoxidized pyrolysis products in smoke naturally falls within definition of smoldering combustion (McKenzie et al., 1995). It might be useful to provide some detail and description of these various processes. It is also important to note that “smoldering” is a complex mixture of multiple processes. For instance, P16 L 308 the authors suggest they aren’t measuring products from smoldering combustion, however, distillation, glowing, and pyrolysis are often grouped into smoldering combustion, therefore where is the evidence you are measuring pyrolysis only? McKenzie, L. M., W. M. Hao, G. N. Richards, and D. E. Ward, Measurement and modeling of air toxins from smoldering combustion of biomass, Environ. Sci. Technol., 29, 2047 – 2054, 1995.

***Author Comments:** We thank the referee for the comment, and we have modified the text to acknowledge that pyrolysis is not “the” first step, but is one of the first steps. As to the second comment, “how do we know the measured gases are pyrolysis only?” The answer to that is we don’t know that the gases are only pyrolysis gases. What we do know and have tried to explain throughout the course of the manuscript is that our imperfect sampling method served as a crude “molecular tweezers” to capture many of the gases prior to onset of combustion. We note the imperfection of the method in the introduction (in the analysis and discussion sections as well) and point out that it does not capture only pyrolysis gases. Still, this paper, to the best of our knowledge, is one of the first field experiments to focus on “early-stage” gas-phase emissions.

Referee Comments: The goal was to sample before the flame front, though it is likely that glowing combustion is also hot enough to drive pyrolysis. Additionally, the high heat release rate associated with flaming combustion likely pyrolyzes more fuels and there is often a peak in pyrolysis products before, during, or shortly after the peak in flaming product. Here the authors are likely probing only a portion of the pyrolysis products as sampling preceded the flame front only. There was no attempt to sample pyrolysis products escaping oxidation in the cool flame interiors or following the flame front. Thus, the “pyrolysis products” measured are likely biased/limited to products specifically sampled during the flame front sampling, and it has been shown in other work that pyrolysis mostly occurs after the flame front driven by the heat of glowing (Yokelson et al. 1996). For these reasons, how representative are the pyrolysis emissions measured here?

Yokelson, R. J., D. W. T. Griffith, and D. E. Ward, Open-path Fourier transform infrared studies of large-scale laboratory biomass fires, J. Geophys Res., 101, 21,067 – 21,080, 1996.

***Author Comments:** The referee is correct in that pyrolysis gases are not associated strictly with the pre-flame front of the fire, but also occur in the flame envelope and after the flame front. As to how well the present measurements represent (largely) pyrolysis gases is worthy of discussion and indeed is open to the interpretation of the reader. What we have attempted to do is capture those (pyrolysis) gases prior to the onset of combustion, as there have been many prior studies focusing on either the combustion or smoldering phases (or both) and few or no field studies focusing on the pyrolysis or other early phases. Further studies to better distinguish / characterize the different early phases of the fire, including pyrolysis, are worthy of research by the atmospheric community.

Referee Comments: It doesn't appear as though there is any temperature data available, thus how can the authors distinguish between "low-temperature" and "high temperature" pyrolysis? The assignment is purely qualitative. Figure 1 only shows temperatures up to 170C. We'd expect in an oxygen-rich environment the biomass is readily ignited around 500- 600C, therefore most "high temperature" pyrolysis experiments are performed in a N2- atmosphere and more accurately report pyrolysis specific compounds. Determining and quantifying pyrolysis products across a range of temperatures and fuels would have been more useful by heating fuels in a laboratory where the FTIR could instead sample directly.

***Author Comments:** Closer inspection of Figure 1 will show that there are in fact several spots in the color coding indicating bright yellow during the flame, and while perhaps difficult to read, the temperature scale at right thus indicates a maximal temperature of 477 °C i.e. nearly 500 °C. We have modified the figure to make the temperature scale more legible in this field experiment.

Referee Comments: There is some discussion about spectral regions used and MALT conditions, however, there is no discussion concerning the uncertainty and LODs of your measurements. While much of this may be discussed in Scharko et al. 2018, there still needs to be some information provided in this manuscript.

***Author Comments:** The present manuscript is already very long, and in the interest of brevity we still feel it appropriate to direct the reader to the Scharko et al. paper for those discussions.

Referee Comments: The detection limits of 12 ppm for acetaldehyde described in the companion paper on this technique are not sensitive enough for most real-world smoke. Do the high LODs of other compounds prevent their detection in this work?

***Author Comments:** It may be that the limits of detection for a few of the compounds are sufficiently high that they do indeed preclude their detection via FTIR; we note that acetaldehyde does not have particularly favorable detection limits due to its strongest band near 1750 cm^{-1} being obfuscated by water and other analytes; it was quantified using the weaker C-H stretching lines near 2716 cm^{-1} and thus sensitive detection for this species is more challenging.

Referee Comments: Similar to whole air sampling canister-based measurements, there needs to be some discussion about the losses of compounds to the walls of the canister, compounds reacting away, as well as gases formed. Could this account for the higher ERs of alkenes such as ethyne? There is a brief mention of wall losses of NH3, and I suspect this is the major reason no ammonia was measured in this study. The authors incorrectly state that the absence of NH3 supports the fact that low-temperature pyrolysis and/or smoldering isn't measured in this study. It would be useful to cite other FTIR measurements and discussions of ammonia wall losses as well as the potential wall losses of other "sticky compounds" (Stockwell et al., 2014; Yokelson et al., 2003). Yokelson, R. J., Christian, T. J., Bertschi, I. T., and Hao, W. M.: Evaluation of adsorption effects 10 on measurements of ammonia, acetic acid, and methanol, J. Geophys. Res., 108, 4649, doi:10.1029/2003JD003549, 2003.

***Author Comments:** We have addressed the referee's valid and well-known concern about the losses of certain compounds reacting away but especially adhering to the walls of the sampling containers in section 3.6, and also added the suggested references.

Referee Comments: How useful is calculating an emission factor, considering the definition of EF is the amount of a compound emitted per unit of dry fuel consumed? If measurements only probe the beginning of the process before any combustion has occurred, then the fuel has not been completely consumed. Does this complicate the use of EFs and the assumptions about the amount of carbon consumed considered in the emission factor calculation?

***Author Comments:** We address the limited utility of EF in the text. The calculation of the EF is indeed of limited scope here for these and other reasons. We have therefore mostly reported ER values.

Referee Comments: P13 L 249 – The authors mention the atmospheric chemistry effects of "total gases emitted during the burns" being the motivation for calculating OH reactivities, however, this is not really an accurate statement as this manuscript is only measuring pyrolysis products preceding combustion. More realistic EFs would be calculated from fire- integrated EFs. Is there other motivation for including a section in the manuscript on OH reactivity?

***Author Comments:** Based on this referee's suggestion and other individuals' comments we have decided to remove the OH reactivity and discussion sections from the main manuscript.

Referee Comments: Eqn 4: Sekimoto et al., 2018 hasn't shown how effective the use of these two proxies are for real-world fires and the equation was designed to predict total VOC emissions. Using this equation to justify sampling of "high temperature" pyrolysis is not supported. Additionally, in Figure 2 how have the authors decided to compare to these particular studies? Would it be more useful to compare to other field studies, instead of using so many laboratory fire-integrated emissions? It may be useful to focus on field studies with similar fuel types or similar burn conditions (e.g. Yokelson et al 2013, Akagi et al., 2013 "late EFs" calculated for smoldering combustions, Bertschi et al., 2003 samples residual smoldering combustion).

***Author Comments:** The fit of the present data to equation 4 and the comparison to the other (fire averaged) studies as seen in Figure 2 was aimed to emphasize precisely that the earlier capture of the (pyrolysis) gases resulted in a very different acetylene/furan ratios.

Referee Comments: How did the authors ensure they weren't getting flaming products from fire-driven flow? C2H2 has been observed to increase with increasing MCE (Burling et al., 2011; Yokelson et al 2008) and it's been noted as a "flaming" compound previously. I understand it can also be produced from smoldering combustion, but what makes the author's certain they are capturing pyrolysis produced C2H2?

***Author Comments:** As addressed above –we are not certain that there is only pyrolysis-produced C_2H_2, there may well be "flaming phase" C_2H_2 captured in our samples as well. Although not discussed in this paper due to length considerations, some of the co-authors on this paper also collected gas samples in canisters from both the flaming and pyrolysis stages and analyzed the canisters using GC; the GC results also showed enhanced ratios of H_2 and CO/CO_2 for samples collected prior to the flame front (i.e. the pyrolysis stage) compared to the gas samples collected during the flaming stage; these measurements provide further evidence that the sampling technique is capturing the gases at a different stage (earlier stage) in the fire.

Referee Comments: It is unclear how useful some of the tables and figures are. The comparisons to previous work seems arbitrary. Some justification for how studies were selected for comparisons are needed.

***Author Comments:** This comment is rather vague, but we have attempted to respond to the referee's comment; we (and referee #1) believe that the tables and figures as a whole are useful. Also, as noted above, we compared to other (fire averaged) studies, e.g. in Figure 2, to emphasize that our technique resulted in very different acetylene/furan ratios. For example, one of the comparisons included a field study involving prescribed burns at the same site in South Carolina.

Technical corrections:

P2 L 39 Should be "biomass burning emissions"

***Author Comments:** The manuscript has been changed to reflect the suggestion.

P3 L 54 More up-to-date citations could be helpful here

Author Comments: We thank this referee as well as referee #1 for the same comment. More up to date citations have been added throughout the introduction.

P3 L 71 Similar to specific comment (2): There is some detailed discussion about the downwind changes in fire emissions measured by FTIR. It's not entirely clear why this is relevant in the discussion as no downwind smoke is measured in this study.

***Author Comments:** We thank the referee for the comment; we have included the discussions about earlier field studies in order to demonstrate how the present work is different from previous studies and our emphasis on collecting gases prior to arrival of the flame front.

P4 L 84 & L 86 I don't think "hotter" and "cooler" is proper terminology. There is quite a range in temperatures in a fire, both in the flame itself and throughout the fuel bed, thus hotter/cooler are relative terms.

***Author Comments:** These adjectives have been dropped.

P4 L 86-87 It might be worth mentioning more OVOCs from smoldering combustion at lower MCE

***Author Comments:** We have modified the text accordingly.

P6 L 126 "attempts to ensure" Please change this phrasing, it is confusing.

***Author Comments:** Sentence changed to "attempts to collect only gases in front of the flame".

P10 L 182 I don't understand the "aliquots"- Does this mean samples in the same canister were all taken from different areas at different times?

***Author Comments:** What we are trying to express is that samples were collected over a short period of time (and area) while keeping the probe in front of the flame to achieve the desired pressure of 138 kPa.

P11 L 204 I'm confused about your H2O and CO2, this wording implies that you did not actually measure these species, though I'm assuming that instead the authors used different spectral regions that weren't optically saturated as values are reported for these compounds later on?

***Author Comments:** Correct: We stated that in order to determine the best associated values we did not use those spectral domains that demonstrated saturated absorptions. See line 220-223

P11 L 212- Instead of relative to any "known gas" it should be relative to a co-emitted, long-lived species. Some discussion to describe that CO and CO2 can be generated during glowing, pyrolysis, and flaming would be useful.

***Author Comments:** We have changed the wording from "known" to "co-emitted, long-lived" gas.

P11 L 216- The background levels of both CO and CO2 likely changed as fuels were burned in the area. I noticed several burns occurred in time fairly close together, but it is not clear whether the authors took into account the possibility of a changing background or if a constant background was assumed. I believe it is the latter, but this likely adds uncertainty to the ERs.

***Author Comments:** This is perhaps true, but likely a minimal effect. First, on all three days there was a period of a few hours between fires that helped dissipate the CO and CO_2 levels. Second, on two of the three days, while in close general proximity the second fire of the day was burned at an upwind location from the first fire.

P11 L224- The authors state these are discrete ERs, however, it seems as though there are several samples in the same canister taken from various areas at various times, "aliquots" as they are described. Because of these sampling preferences, is this really a "discrete" sample and how comparable are these to other more traditional grab "snapshot" samples generally seen when sampling with canisters?

Author Comments: As already stated, the samples were collected over a short period of time and area while keeping the probe in front of the flame and near vegetation. This collection is different than other studies since the probe is always positioned ahead of the flame front and is not collecting an average over all the stages of the fire; instead the gases are collected near a plant species before the flame has reached it. The use of the word "discrete" is to highlight this difference in which we are trying to only capture gases from one stage of the burn, .i.e. prior to the onset of combustion; of course, as already stated, contributions from flaming emissions may also be present albeit at lower levels.

P12 L 230 also reference Ward and Radke, 1993 Ward, D. E., and L. F. Radke, Emissions measurements from vegetation fires: A comparative evaluation of methods and results, in Fire in the Environment: The Ecological, Atmospheric and Climatic Importance of Vegetation Fires, edited by P.J. Crutzen and J. G. Goldammer, pp. 53 – 76, John Wiley, New York, 1993

Author Comments: We thank the referee and have added the reference.

P12 L 243- Stockwell et al. 2015 found these underestimates can be higher for certain fuel types Stockwell, C. E., Veres, P. R., Williams, J., and Yokelson, R. J.: Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry, Atmos. Chem. Phys., 15, 845–865, https://doi.org/10.5194/acp-15845-2015, 2015

Author Comments: We thank the referee for this comment; we have modified the text and have added the citation.

P13 L 260 This first sentence is not entirely accurate. The combustion efficiency equation is designated to describe combustion chemistry and Sekimoto shows that MCE doesn't necessarily describe their VOC emission profiles. It is true that MCE does not correlate with products as well for pure smoldering, especially for grab samples or in real time, because the same MCE may characterize different white smoke/glowing ratios. MCE is most useful when there is a range of flaming/smoldering as is common in most real-world fires, however, this is not the case in this manuscript.

***Author Comments:** We would argue that Sekimoto's description is relevant to the text, namely that the CE or MCE is really not the best metric, as it is a measure of the degree of combustion (hence the name) and the gases that we measure (as for pyrolysis gases as Sekimoto also suggests), are captured before the onset of combustion, rendering the MCE a "less appropriate" metric.

P16 L308- The authors state: "the lower MCE values do not represent the fire burning in the smoldering stage" This is an unsupported claim and as I mentioned earlier smoldering is a grab bag for various processes that include distillation, glowing, and pyrolysis.

***Author Comments:** We have partially modified this sentence and point out that the latter part of the sentence clarifies: "but rather suggest that pyrolysis products were captured (at least in part) prior to the onset of combustion."

P16 L 311 This may be a good area to mention fire-driven flow P17

***Author Comments:** We are not sure how to interpret this comment. We have added entrainment as a mechanism to incorporate more atmospheric air into the region of sampling as well as the challenge of capturing gases of a moving target.

Figure 2: where are the study average MCEs?

***Author Comments:** As discussed, the MCEs are of lesser utility to his study of early-phase non-combustion processes. The study average MCE is found in the title of Table 2. The geometric mean is the most appropriate (of arithmetic, geometric and harmonic) measure of central tendency for ratios such as MCE (Clark-Carter, 2005).

P18 L 336- What was the range of CO2 emissions? If only a narrow spread, this might explain the lower correlation coefficients for something like C2H2 with CO2.

Author Comments: The range of CO_2 emissions are found in the supplemental material, and generally represent a moderate spread of values.

Table 3. Stockwell et al 2015 has a more complete list of compounds measured including acetaldehyde, acetone, etc. Stockwell, C. E., Veres, P. R., Williams, J., and Yokelson, R. J.: Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry, Atmos. Chem. Phys., 15, 845-865, https://doi.org/10.5194/acp- 15-845-2015, 2015.

***Author Comments:** This paper has been cited, along with 24 others by Yokelson et al.

P29 L 531 The fuel type and N-composition certainly influences HCN emissions, however, it is random to highlight Indonesian peat here, this is a very unique fuel type and peat burns by smoldering combustion only, thus it follows that the fuel N is biased towards HCN rather than flaming products such as NO_x. Not sure it is worth mentioning in this manuscript.

***Author Comments:** It is indeed somewhat random to reference the values from Indonesian peat measurements, but the Indonesian peat values are truly are unique/anomalous and are thus worthy of the fleeting reference.

P31 L 555 the authors argue NH_3 is only present in the smoldering phase. I'd argue you did measure some smoldering combustion and the most likely for no NH3 detection is wall losses in the canisters as I discussed in specific comment (9).

***Author Comments:** This was addressed above. However, we also have OPAG and other data where we clearly do see NH_3 in the smoldering stage but not in the earlier stages. This does not mean that wall loss adhesion problems do not exist, but other data does show reduced ammonia and amines in the earlier stages relative to smoldering. These studies will be published in the near future.

The text that has been changed in seen in the revised manuscript below in red font.

Gas-Phase Pyrolysis Products Emitted by Prescribed Fires in Pine Forests with a Shrub Understory in the Southeastern United States**

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ABSTRACT

In this study we capture and identify pyrolysis gases from prescribed burns conducted in pine forests with a shrub understory using a manual extraction device. The device selectively sampled emissions ahead of the flame front, minimizing collection of oxidized gases, with the captured gases analyzed in the laboratory using infrared absorption spectroscopy. Results show that emission ratios (ER) relative to CO for ethene and acetylene were significantly greater than previous fire studies, suggesting that the sample device was able to collect predominantly gases generated prior to ignition. Further evidence that ignition had not begun was corroborated by novel infrared detections of several species, in particular naphthalene. With regards to oxygenated species, several aldehydes (acrolein, furaldehyde, acetaldehyde, formaldehyde) and the carboxylic acids (formic, acetic) were all observed; results show that ERs for acetaldehyde were noticeably greater while ERs for formaldehyde and acetic acid were lower compared to other studies. The acetylene-to-furan ratio also suggests that high temperature pyrolysis was the dominant process generating the collected gases.

1. INTRODUCTION

Biomass burning contributes large quantities of trace gases into the earth's atmosphere (Crutzen and Andreae, 1990; Akagi et al., 2011; Andreae and Merlet, 2001; Crutzen et al., 1979; Yokelson et al., 2013b; Andreae, 1991). The primary carbon-containing gases emitted during such burns are CO_2, CO and CH_4, in order of decreasing concentration (Ward and Hardy, 1991). Hundreds of other trace gases have also been identified in the emissions, including many non-methane volatile organic compounds (NMVOCs), oxygenated volatile organic compounds (OVOCs), nitrogen-containing species and sulfur compounds (Yokelson et al., 1996; Lobert et al., 1991; Talbot et al., 1988). The major sources of such biomass burning emissions are wildland (WF) fire and, to a lesser extent, prescribed fire (PF). Prescribed fires are used to reduce dangerous fuel buildups and manage habitats (Fernandes and Botelho, 2003). The use of prescribed fire as a preventative tool is of particular importance in the western United States (U.S.) where wildland fires are increasing in severity (Turetsky et al., 2011; Miller et al., 2009). In the southeastern U.S., prescribed fire is also used on a routine basis for purposes such as ecosystem management (Waldrop and Goodrick, 2012). For these and other beneficial reasons, an estimated 3.6 million hectares of forestry land have been burned in the U.S. by prescribed fire each year (Melvin, 2012). Agencies that conduct such burns often rely on fire-related models (Reinhardt et al., 1997; Prichard et al., 2006) to predict the impacts of the prescribed burn. Models and experience are used to determine desired fire behavior from fuel, weather, and topography in order to achieve the desired fire effects. The current operational model to predict fire behavior uses a simplistic approach to the chemical aspects of combustion and fire spread (Albini, 1976; Rothermel, 1972). Physics-based fire behavior models, while not currently fast enough for operational use, have the ability to incorporate details of fire behavior including heat transfer and chemical reactions (Clark et al., 2010; Mell et al., 2009). These models, such as FIRETEC and FDS, often model the process of pyrolysis based on results for wood or ground foliage samples. In order to improve the modeling of pyrolysis and combustion in these models, a study is currently underway (Weise et al., 2018) wherein pyrolysis products from the same plant species are being measured in 1) oxygen-free environment using intact foliage samples (Amini et al., 2019a; Amini et al., 2019b; Safdari et al., 2019; Safdari et al., 2018), 2) in an atmospheric oxygen wind tunnel setting with relatively simple heterogeneous fuel beds (paper in preparation), and 3) in small field burns (this manuscript). One of the goals of the larger study is to determine the relationship between the controlled lab results and actual fire conditions in the field as was done previously by Yokelson et al. (2013a), that study focusing mostly on the flaming and smolder stages. While the present study focuses only on early stage emissions, including pyrolysis, hopefully such data can indirectly improve our understanding of the fire processes. Detailed knowledge of the pyrolysis products and other early-stage processes will ultimately improve our ability to model fire behavior (Ferguson et al., 2013; Shotorban et al., 2018; Yashwanth et al., 2016).

Due to the influential role of wildland fire on atmospheric chemistry and climate, there has been considerable interest in identifying and quantifying gas emissions from fire as studied both in the laboratory and in field burns (Crutzen et al., 1979; Andreae et al., 1988; Lobert et al., 1991; Andreae et al., 1994; Lindesay et al., 1996; Goode et al., 1999; Yokelson et al., 1999; Yokelson et al., 1996; Chi et al., 1979). The type of gases emitted and their relative abundances depend on many factors such as fuel type, fuel arrangement, land management activities, burning techniques and environmental conditions (Ward et al., 1996; Ward et al., 1992). In the 1990s, Griffith, Yokelson and co-workers conducted a series of laboratory studies using an open-path Fourier transform infrared (FTIR) spectrometer to investigate how some of these factors influence the emitted gases (Goode et al., 1999; Yokelson et al., 1996; Yokelson et al., 1997). There have been several follow-on laboratory studies using IR spectroscopy along with other analytical techniques to identify previously unknown fire emission products and to derive emission factors from various fuel types (Burling et al., 2010; Hatch et al., 2017; Selimovic et al., 2018; Stockwell et al., 2014b; Yokelson et al., 2013b; Gilman et al., 2015).

In addition to the laboratory studies, a number of field campaigns have also used FTIR spectroscopy to identify trace gases from prescribed fires (Akagi et al., 2013; Burling et al., 2011b; Akagi et al., 2014; Goode et al., 2000; Yokelson et al., 1999; Wooster et al., 2011; Alves et al., 2010; Hurst et al., 1994a; Hurst et al., 1994b; Paton-Walsh et al., 2010; Paton-Walsh et al., 2008; Guérette et al., 2018). Studies that have the ability to measure emissions both near the fire and aloft are especially useful in understanding the complex chemistries that occur during and after prescribed fires, including the (oxidative) chemistry of the downwind plume. For example, (Akagi et al., 2013) detected limonene from a prescribed burn with a land-based FTIR and linked it to the production of ozone, formaldehyde and methanol, all of which were measured downwind with an airborne-based FTIR. In an earlier prescribed burn study, Burling et al. (2011a) detected enhanced levels of isoprene and 1,3-butadiene in the smoke from a living tree when compared to dead stumps under the same conditions. Emission characteristics obtained during such campaigns can be especially useful for the implementation or verification of effective burning techniques to minimize the gases released during prescribed burns. However, few investigations have studied the pre-ignition or pyrolysis gases emitted prior to the flaming combustion stage. While it is clearly important to sample non-laboratory fires, it must also be borne in mind that there are significant differences in the emissions between WF and PF, such as the PF work reported here. As pointed out by Liu et al. (2017) as one example, there is far more particulate matter emitted from a WF than for a controlled PF. Other differences in emissions from PF and WF must surely exist, e.g. fuel consumption, fire meteorology. This paper only explores gas-phase emissions of the early stages of PF in the southeastern U.S.

The present study differs from earlier works in that we exclusively attempt to investigate pyrolysis, which is one of the first steps in the burning process (Collard et al., 2014); in particular we investigate the gas-phase pyrolysis species generated during prescribed burns. Primary mechanisms associated with pyrolysis of biomass are char formation, depolymerization and species fragmentation. Volatile products are generated and, if unstable, can continue to undergo secondary (non-combustion) reactions such as cracking or recombination (Collard and Blin, 2014). Pyrolytic reactions produce fuel gases that, if sufficient in quantity and in the presence of oxygen, will maintain the flame via combustion pathways (Ward and Hardy, 1991; Di Blasi, 1993). The primary objectives of the present study are thus a) to detect pyrolysis gases in prescribed burns (i.e. gases emitted prior to the flame front and prior to onset of combustion) and b) to determine if they differ from the pyrolysis gases measured under more tightly controlled laboratory conditions.

There have in fact been many pyrolysis laboratory studies carried out in controlled environments: In one of the earliest investigations, DeGroot et al. (1988) detected H_2O, CO_2, CH_3OH, HCOOH and CH_3COOH from the pyrolysis of wood. More recent studies have observed several other compounds, such as CO, CH_4, lightweight hydrocarbons (C_2–C_5) and light tar compounds (e.g. benzene and its derivatives and polycyclic aromatic hydrocarbons) from the slow pyrolysis of Birch wood (Fagernäs et al., 2012). Oxygenated compounds (e.g. furan-related compounds) have been observed from the fast pyrolysis of levoglucosan, a known pyrolyzate of cellulose (Bai et al., 2013). Laboratory experiments that have investigated condensed and/or gas phase compounds generated by pyrolysis under controlled conditions have revealed that the speciation and distribution of the products are dependent on a number of factors such as heating rate, temperature, fuel composition, live vs. dead fuels and amount of available oxygen (Azeez et al., 2011; Lu et al., 2011; Shen et al., 2010; Safdari et al., 2018; Ren and Zhao, 2012, 2013a, b). For instance, Ren and coworkers (2013a) found that the amount and speciation of nitrogen containing pyrolyzates is complicated and influenced by the content of mineral matter, the presence of oxygen (Ren and Zhao, 2012), as well as the structure (e.g. aliphatic vs. heterocyclic) of the amino acids and the amount of cellulose, hemicellulose and lignin in the sample. Similarly, the release of oxygenated compounds (e.g. phenolic compounds) from the pyrolysis of lignin is sensitive to the presence of oxygen (Kibet et al., 2012). The pyrolysis studies mentioned above were conducted in controlled settings or on smaller scales. There remains a paucity of data that identify and quantify gas-phase pyrolysis species emitted from actual prescribed burns at the field scale.

To our knowledge, this is one of the first field studies that discriminatively measures pyrolysis and early-phase gases for southeastern U.S. fuels. Isolating such species is indeed challenging as they often blend with the background atmosphere and are rapidly mixed with other gases at the onset of combustion. One must thus isolate the “pyrolysis molecules” either optically, mechanically or temporally. In this study, we selectively probe the pyrolysis gases by using a simple manually-operated spatial collection device that attempts to collect only gases in front of the flame. While not a perfect solution, the information gathered in this study adds important insights into the primary products generated during the pyrolysis process.

2. EXPERIMENTAL

2.1 Site description

During the week of 29 April 2018, a total of seven small plots (450 to 900 m^2) were burned using prescribed fire at Ft. Jackson, South Carolina (SC), latitude: 34.05 and longitude: –80.83, approximately 10 km east of Columbia, SC. The fort lies entirely within the Sandhills ecosystem in the South Carolina coastal plain, which runs approximately parallel to the Atlantic Ocean coast, 175 km inland. The Sandhills region thus forms a belt that tracks southwest – northeast across sands of varying depth with a high content of pure silica (Porcher and Rayner, 2001). The deep sands support an overstory vegetation that has significant amounts of turkey oak (*Quercus laevis* Walter) and two native pine species relatively unique to the southeastern U.S.: longleaf pine (*Pinus palustris* Mill.) and slash pine (*Pinus elliottii* Engelm.). The understory has substantial quantities of immature turkey oak, longleaf and slash pine, along with sparkleberry (*Vaccinium arboreum* Marshall) and a heterogeneous organic layer of woody material, litter, duff and cones atop the mineral soil. The longleaf ecosystem depends on fire for maintenance (Cary, 1932). Site details for the seven burn plots, all with a 2 year rough (i.e. burned 2 years prior), are summarized in Table 1. Eight pre- and post-fire 1.0 meter square biomass clipped plots were established at each 160 m^2 research block within the larger burn plots where organic vegetative material was collected before and after each fire. Shrub, grasses/forbs, down woody material (0-0.6, 0.6-2.5, 2.5-7.6, 7.6-22.9 cm in diameter), litter and duff, are the major fuel bed components that were targeted. Fuel moisture samples for each major component were collected before ignition to determine fuel moisture content for each fuel bed component. Figure 1 shows photographs of site 16, plot 1 before, during and after the burn as well as a thermal image of the flame interacting with the fuel.

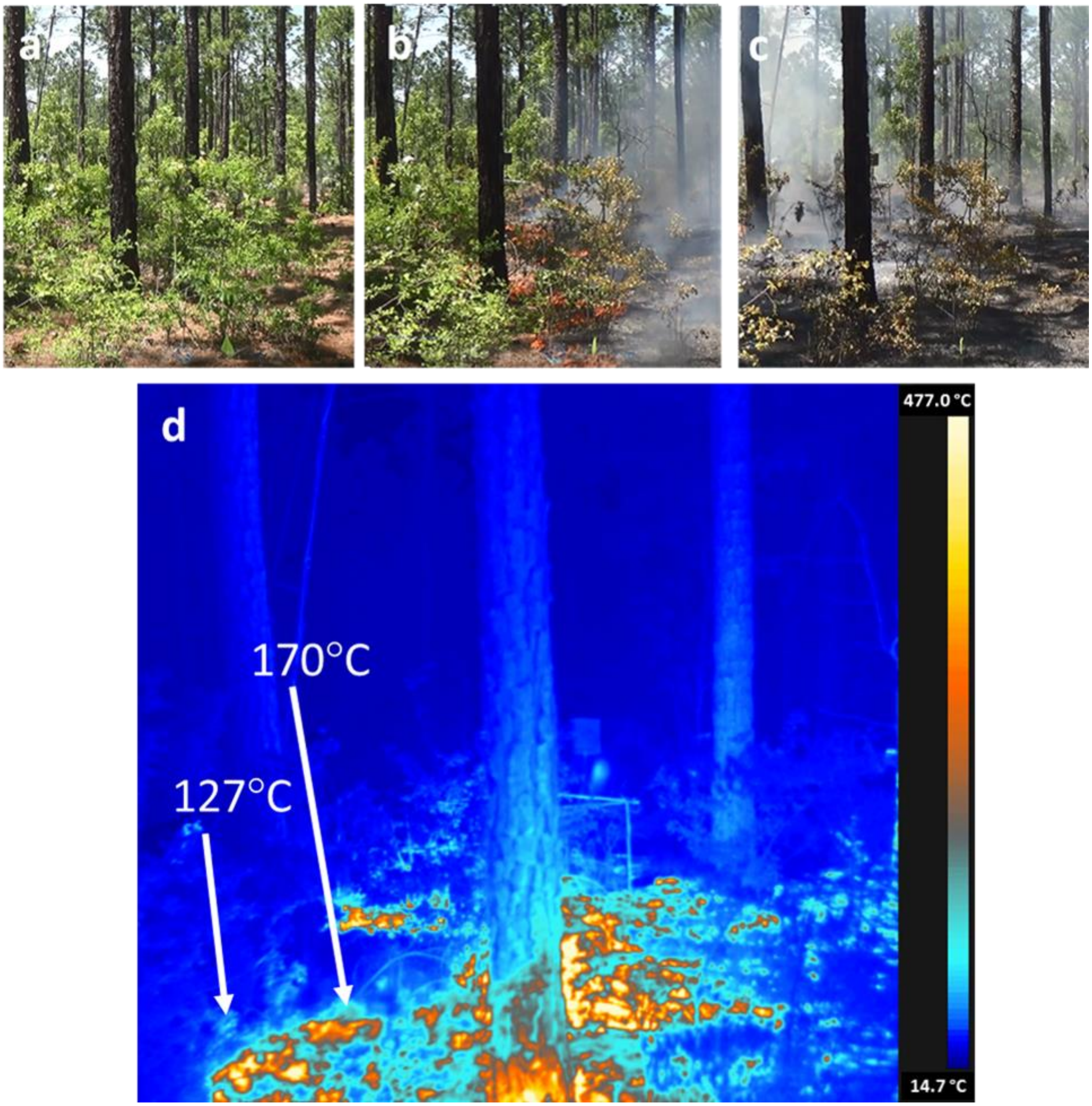

Figure 1. Photographs of site 16, plot 1 on 3 May 2018 between 14:00 and 14:40 local time. The plot (a) before the flame, (b) while the flame interacted with the fuel at 14:33 and (c) smoldering combustion of the fuel. The primary species seen in the understory for this burn plot are sparkleberry and a litter layer of pine needles. (d) Thermal image of the flame interacting with the fuel at time of 14:33.

Table 1. Plot name, date/time, fuel description, atmospheric conditions (all clear sky days) and plot mixing height and area for the prescribed burns.

Burn plot	Date (2018)	Local start time (EDT)	Local finish time (EDT)	Dominant overstory	Understory fuels	Ambient temperature (°C)	Relative humidity (%)	Surface winds (m s^{-1}) and wind direction	Mixing height (m)	Area burned (m^2)
24B-triangle	1-May	12:11	12:37	slash pine	sparkleberry/ logs	24	26	2.7 SW	975	450
24B-north diamond	1-May	13:53	14:43	slash pine	sparkleberry/ logs	28	18	2.7 SW	1310	900
24A-square	2-May	9:37	10:22	longleaf pine	sparkleberry/ duff	21	53	2.7 SW	792	900
24A-triangle	2-May	12:08	12:43	longleaf pine	sparkleberry/ duff	27	34	2.7 SW	1189	450
16 plot 5	3-May	9:39	10:21	longleaf pine	sparkleberry/ bracken fern	22	59	2.7 SW	579	900
16 plot 6	3-May	11:44	12:13	longleaf pine	sparkleberry/ turkey oak	26	43	3.1 SW	1067	900
16 plot 1	3-May	13:56	14:41	longleaf pine	sparkleberry/ turkey oak	29	30	3.1 SW	1494	900

2.2 Collection device

Our approach to sampling used an extractive collection device whose tube inlet sampled air and emissions directly ahead of the flame. This simple solution is similar to other canister methods often used with gas chromatographic analysis (Young et al., 1997) and also conceptually similar to the land-based FTIR used to sample emissions as described by Akagi et al. (2013, 2014) and Burling et al. (2011). The canister sampling package, mounted on a metal frame, contained a set of evacuated canisters which were carried to the individual burn plots. The sampling package consisted of a 12-Volt Swing Piston KNF Neuberger Pump (NPK09DC) plumbed with stainless steel tubing to a pressure relief valve and gauge. The pressure relief valve was adjustable to regulate the pressure of the system and ultimately the fill pressure of the canisters. The flow rate to fill the canisters was 15 liters min^{-1}. A sampling probe (2.5 m of 6 mm stainless steel tubing plus 2 m of flexible stainless-steel line) was attached to the inlet of the package to collect pyrolysis gases from point sources of vegetation within the burning plots. The device had an in-line two-way valve to control the sampling interval. To capture a pyrolysis sample, the probe was placed near the base of the flame, immediately above the fuel where the pyrolysis gases should be emitted at maximal levels. Seven to ten aliquots of gas sample were added to a single canister as the device was moved in front of the flame to capture pyrolysis gases. Each 3-liter Summa canister was filled to approximately 138 kPa (20 psia) for the FTIR analysis.

2.3 FTIR Spectrometer and Spectral Analysis

Experimental details regarding FTIR measurement and ensuing spectral analysis procedures have been previously reported (Scharko et al., 2019), but are briefly summarized as follows: Gases in the canisters were returned from the field to the laboratory and analyzed the same day or the following day using an 8 meter White cell (Bruker A136/2-L) and FTIR; canisters were connected to the gas cell via 3/8” stainless steel tubing with both the tubing and gas cell heated to 70 °C to prevent analyte adhesion. The cell was coupled to a purged FTIR spectrometer (Bruker Tensor 37) equipped with a glow bar source, KBr beamsplitter and liquid-N_2-cooled mercury cadmium telluride detector. Spectra were collected from 4000 to 500 cm^{-1} at 0.6 cm^{-1} resolution. Spectral analysis was carried out using the MALT5 program (Griffith, 2016) and 50 °C reference spectra from the PNNL database (Sharpe et al., 2004; Johnson et al., 2010) as well as absorption lines from HITRAN (Gordon et al., 2017). MALT5 fits the assigned reference spectral lines to the measured spectrum by optimizing the fit of all gases ascribed to the spectral window and minimizing the residual. The calculation involves input parameters such as path length, resolution and apodization accompanied by reference absorption cross-sections and the measured spectrum with its associated temperature/ pressure values. Both H_2O and CO_2 had peaks that were saturated; these regions were eliminated from analysis. In some instances, peaks for the gases of interest were also saturated in which case the pressure in the gas cell was reduced and the measurement repeated.

2.4 Calculation of emission ratios and emission factors

A convenient quantity to compare emissions between burns is the emission ratio (ER). This ratio is calculated by the change in the analyte of interest relative to the change in a co-emitted, long-lived gas, typically CO or CO_2. For the present study, the change in analyte is divided by the change in CO:

$$ER = \left(\frac{\Delta\text{analyte}}{\Delta\text{CO}}\right). \qquad (2)$$

It is important to note that these are the changes in analyte and CO relative to background atmosphere (i.e. relative to ambient "clean air" conditions). The background levels of CO and CO_2 were measured using an open path gas analyzer (OPAG 22) prior to the series of burns. The initial CO_2 level was measured to be 409 ppm (this value agrees with the global averaged CO_2 for May 2018 of 408.7 ppm (Dlugokencky and Tans)) whereas the CO level was often below the OPAG detection limit. [Due to challenging experimental conditions and moderate CO band intensities, the OPAG detection limit was poor for these CO measurements and could not achieve 200 ppb detection limits.] Without an instrument to measure ambient CO with sufficient sensitivity we chose 200 ppb for an estimated background level which is within the range for a typical CO mixing ratio (Seinfeld and Pandis, 2012). Note that the 200 ppb value is sufficiently small that it has negligible effect on the calculated Δanalyte/ΔCO ratios. Emission ratios can be calculated for a single point in time during the fire or they can incorporate the full length of the fire. The present ERs were calculated based on the contents of the individual canisters and represent discrete ERs. Other studies have obtained fire-integrated ERs, which integrate over the entire duration of the fire (Koss et al., 2018) or fire-averaged ERs determined from the slope of the regression with the intercept set to zero (Yokelson et al., 1999).

Another useful quantity is the emission factor (EF), defined as the number of grams emitted of a given analyte per kilogram of dry fuel consumed and estimated using the following equation (Yokelson et al., 1999; Ward and Radke, 1993):

$$\mathrm{EF}\ (\mathrm{g\ kg^{-1}}) = \mathrm{F_{carbon}} \times 1000 \times \frac{\mathrm{MW_{analyte}}}{\mathrm{MW_{carbon}}} \times \frac{\frac{\Delta\mathrm{analyte}}{\Delta\mathrm{CO_2}}}{\sum_{j=1}^{n}\left(\mathrm{NC}_j \times \frac{\Delta\mathrm{C_j}}{\Delta\mathrm{CO_2}}\right)} \tag{3}$$

where F_{carbon} is the mass fraction of carbon in the fuel, $MW_{analyte}$ and MW_{carbon} are the molar masses of the analyte and carbon, respectively, $\frac{\Delta\mathrm{analyte}}{\Delta\mathrm{CO_2}}$ is the emission ratio of the analyte relative to CO_2, $\frac{\Delta\mathrm{C_j}}{\Delta\mathrm{CO_2}}$ is the emission ratio of species *j* relative to CO_2 and NC_j is the number of carbons in species *j*. Note that ΔCO_2 cancels out in equation 3. Elemental analysis of similar southeastern fuels was reported in a previous study (Safdari et al., 2018), and the average carbon content by mass for longleaf pine foliage and litter as well as sparkleberry was 0.52 which was used for F_{carbon}. One assumption in equation 3 is that all of the carbon in the fuel is released and accounted for in the measurements of the *j* carbon species. Most carbon emissions are in the form of CO_2, CO or CH_4. It should be noted that the EF quantities reported here include only compounds measured by the FTIR, and EF values may be overestimated by 1- 2% for most fuels due to undetected carbon species (Akagi et al., 2011). Fuels such as peat or sugar cane may be overestimated by 2−7.5%; it is important to note that the fuel quantity and structure within frequently-burned longleaf pine stands are appreciably different from peat and commercial sugar cane plantations.

3. RESULTS AND DISCUSSION

3.1 Estimating the contribution from high and low temperature processes

Modified combustion efficiency (MCE) uses the excess CO and CO_2 values to quantify the degree of combustion that has occurred in a given smoke plume and the MCE will be discussed below. However, in a recent study Sekimoto et al. (2018) suggested that MCE may not be the best quantity to adequately describe pyrolysis, but rather that emissions of volatile organic compounds (VOCs) from biomass burning may be correlated with high and low temperature pyrolysis factors obtained by carrying out positive matrix factorization (PMF) analysis on the emission profiles. The authors further suggested that the ratio of acetylene (C_2H_2) to furan (C_4H_4O) could be used to estimate the high and low temperature pyrolysis factors. They used the emission profiles from the analysis of 15 different fuels to calculate the following ratio that estimates the high and low temperature VOC emissions:

$$\frac{(\text{Total VOC})_{\text{High T}}}{(\text{Total VOC})_{\text{Low T}}} = \frac{C_2H_2 \,/\, 0.0393}{C_4H_4O \,/\, 0.0159}. \tag{4}$$

We have adopted this estimation approach and have used the acetylene to furan ratio to assess the relative contributions from high and low temperature processes. The average results are displayed in Figure 2 alongside the results from Koss et al. (2018), Gilman et al. (2015) and Akagi et al. (2013). For comparison purposes, the values displayed in Figure 2 were determined using average ERs for acetylene and furan. The present results (right-most bar) are approximately an order of magnitude greater than all previous studies, likely due to the timing of collection and the sampling probe's proximity to the flame. The juxtaposed values from the previous studies were obtained using either a) fire-integrated ERs, b) discrete ERs sampled every 20 to 300 sec or c) fire-averaged ERs, all of which incorporate several different phases of the fire as compared to the present measurements which represent phase-isolated samples just seconds before the flame front. Using the Sekimoto et al. estimation approach, higher acetylene/furan ratios indicate a greater contribution from the high temperature process. The markedly high ratio observed in this study suggests that samples were collected when high temperature pyrolysis was indeed the dominant process. This observation is consistent with the time profile for the contribution of the high temperature pyrolysis factor presented by Sekimoto et al. (2018), which demonstrates that the contribution from high temperature pyrolysis [High-T / (High-T + Low-T)] can easily exceed 0.95 in the early stages of fire, but reduces to smaller fractions (≤ 0.3) in the latter stages. Another key difference is that the sampling probe used at Ft. Jackson was positioned so as to extract gases directly before the flame front, yet in close proximity to it, in order to limit further reactions. In particular, if the highly flammable acetylene molecules were captured prior to subsequent oxidation reactions, this would explain the enhanced ratio of high-to-low-temperature VOC emissions as seen in Figure 2.

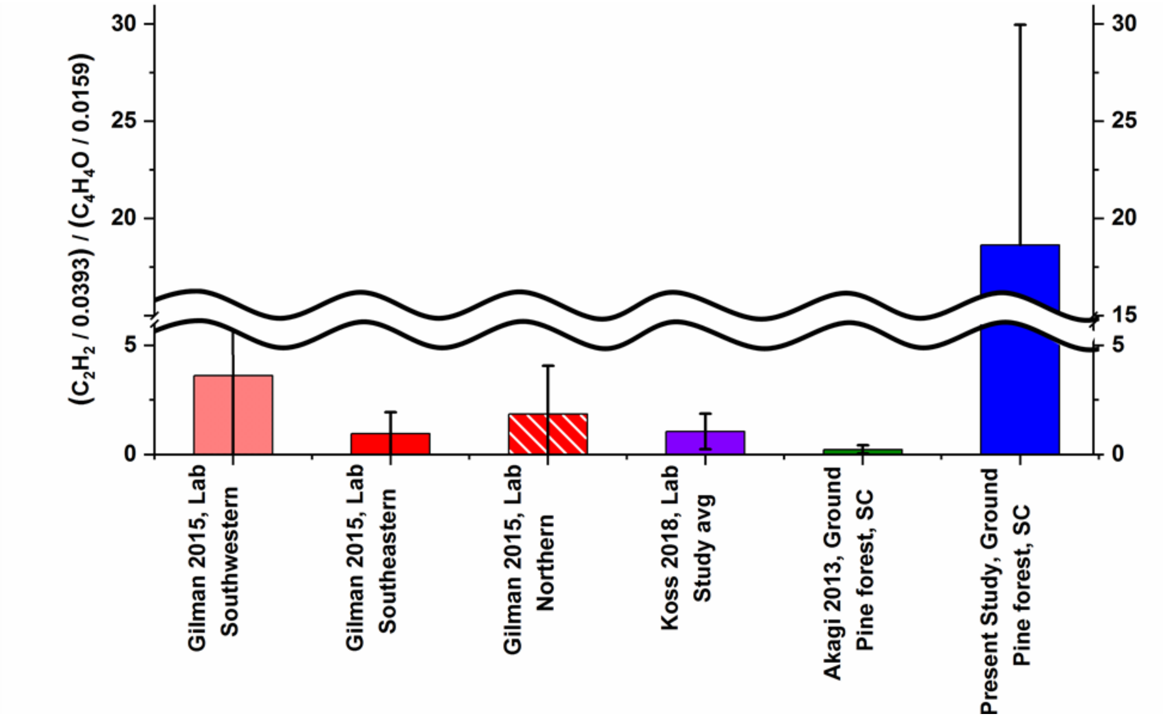

Figure 2. Ratio of acetylene (C_2H_2)/0.0393 to furan (C_4H_4O)/0.0159 to predict the ratio of high to low temperature VOC emissions as outlined by Sekimoto et al. (2018). Error bars represent 1σ. For the present study average results were determined from the 10 collected samples preceding the flame front for acetylene and furan. Koss et al. (2018) values were fire integrated while Gilman et al. (2015) used 20-300 sec integrations. Akagi et al. (2013) reported EFs which were used to calculate ERs for acetylene and furan.

3.2 CO_2 and CO Emissions and MCE Values

As expected, other than H_2O vapor, CO and CO_2 were the predominant gases observed as emissions. Table 2 displays the EF (g kg^{-1}) and ER (ppb/ppm$_{CO}$) values averaged for the ten field measurements. Most prescribed burn studies have focused only on the flaming and smoldering stages. The flaming stage is characterized by more oxidized products and a higher modified combustion efficiency (e.g. 0.85 - 0.97 for flaming) (Ward and Hao, 1991), with MCE defined as:

$$\mathrm{MCE} = \left(\frac{\Delta CO_2}{\Delta CO_2 + \Delta CO}\right). \quad (1)$$

The smoldering phase with lower MCE values (typically ranging from 0.65–0.85) (Urbanski, 2013) displays more non-oxidized (or less-oxidized) species but with a greater fraction of OVOCs observed. The arithmetic mean MCE and standard deviation for all ten measurements at Ft. Jackson was 0.829 ± 0.044. Such MCE values would normally characterize data gathered during smoldering combustion where a combination of processes such as pyrolysis along with glowing combustion of char take place (Yokelson et al., 1997). Higher MCE values are associated with the flaming stage (~0.99 for pure flaming) and indicate more efficient combustion (i.e. a higher reaction temperature and more complete oxidation of the organic matter, while lower values (~0.65-0.85) are associated with the smoldering stage (Urbanski, 2013). Since the present study was aimed at collection of pyrolysis gases preceding the flame front, characterizing the results in terms of MCE values may not be appropriate: The lower MCE values do not represent the fire being in the smoldering stage, but rather suggest that pyrolysis and other early-phase process gases were captured (at least in part) prior to the onset of combustion. As noted, the methodology used with this collection device ideally extracted the pyrolysis gases before they combusted. Due to the proximity of these gases to the flame and the surrounding atmosphere, however, entrainment of air into the region of sampling were likely captured along with pyrolysis gases. As we were sampling a moving zone, some combustion products were thus also likely captured in the region of sampling.

Table 2. Study averages of EF (g kg^{-1}) and ER (ppb/ppm_{CO}) for the ten pyrolysis measurements along with standard deviation (SD). The SD represent the variation for the ten non-identical measurements. For the study averages, the arithmetic mean MCE was found to be 0.83 ± 0.04.

Species	**Formula**	**EF Study Average (g kg^{-1})**	**SD**	**ER Study Average (ppb/ppm_{CO})**	**SD**
Carbon dioxide	CO_2	1469	113	5190	1450
Carbon monoxide	CO	191	45	1000	n/a
Methane	CH_4	11.2	3.9	101.3	18.7
Ethane	C_2H_6	1.14	0.42	5.54	1.48
Ethene	C_2H_4	11.8	3.8	61.1	9.6
Acetylene	C_2H_2	7.4	3.1	40.9	10.4
Propene	C_3H_6	2.69	1.04	9.32	2.34
Allene	C_3H_4	0.30	0.12	1.09	0.23
1,3-Butadiene	C_4H_6	1.20	0.72	3.13	1.25
Isobutene	C_4H_8	0.23	0.15	0.58	0.31
Isoprene	C_5H_8	0.63	0.90	1.18	1.43
Naphthalene	$C_{10}H_8$	0.65	0.36	0.77	0.47
Formaldehyde	HCHO	0.76	0.98	3.63	4.57
Methanol	CH_3OH	1.39	1.40	6.11	5.56
Formic acid	HCOOH	0.23	0.14	0.74	0.42
Acetaldehyde	CH_3CHO	2.84	1.41	9.35	3.59
Acetone	$(CH_3)_2CO$	1.15	0.77	2.92	1.78
Acetic acid	CH_3COOH	1.45	2.66	3.46	6.15
Acrolein	C_3H_4O	1.59	1.01	4.10	2.15
Furan	C_4H_4O	0.41	0.25	0.89	0.49
Furaldehyde	C_4H_3OCHO	1.01	1.01	1.45	1.31
Hydrogen cyanide	HCN	1.34	0.31	7.34	1.25
Nitrous acid	HONO	0.10	0.16	0.30	0.46
Methyl nitrite	CH_3ONO	0.41	0.32	1.06	0.90

3.3 Emissions of Lightweight Hydrocarbons

Besides CO and CO_2, the second most abundant class of gases generated during the prescribed burns was lightweight hydrocarbons (HCs). The lightweight HCs detected by the FTIR include methane, ethane, ethene, acetylene, propene, allene, 1,3-butadiene, isoprene and isobutene. Most of have been previously identified in fire emissions using FTIR either in laboratory experiments (Burling et al., 2010; Christian et al., 2003; Christian et al., 2004; Gilman et al., 2015; Goode et al., 1999; Hatch et al., 2017; Selimovic et al., 2018; Stockwell et al., 2014b; Yokelson et al., 1996; Yokelson et al., 1997) or field settings (Akagi et al., 2013; Akagi et al., 2014; Alves et al., 2010; Burling et al., 2011b; Goode et al., 2000; Hurst et al., 1994a; Hurst et al., 1994b; Karl et al., 2007; Paton-Walsh et al., 2010), the present experiment being first IR detection of allene (Scharko et al., 2019). Figure 3 shows the individual correlations between these lightweight HCs and excess CO mixing ratios. The analyte vs. ΔCO correlation coefficients range from 0.97 (ethene and allene) to 0.66 (isoprene and isobutene). In all cases, the correlation coefficients were larger with CO than with CO_2. Positive relationships have been observed for CO correlations in previous burning studies (Hurst et al., 1994a; Hurst et al., 1994b).

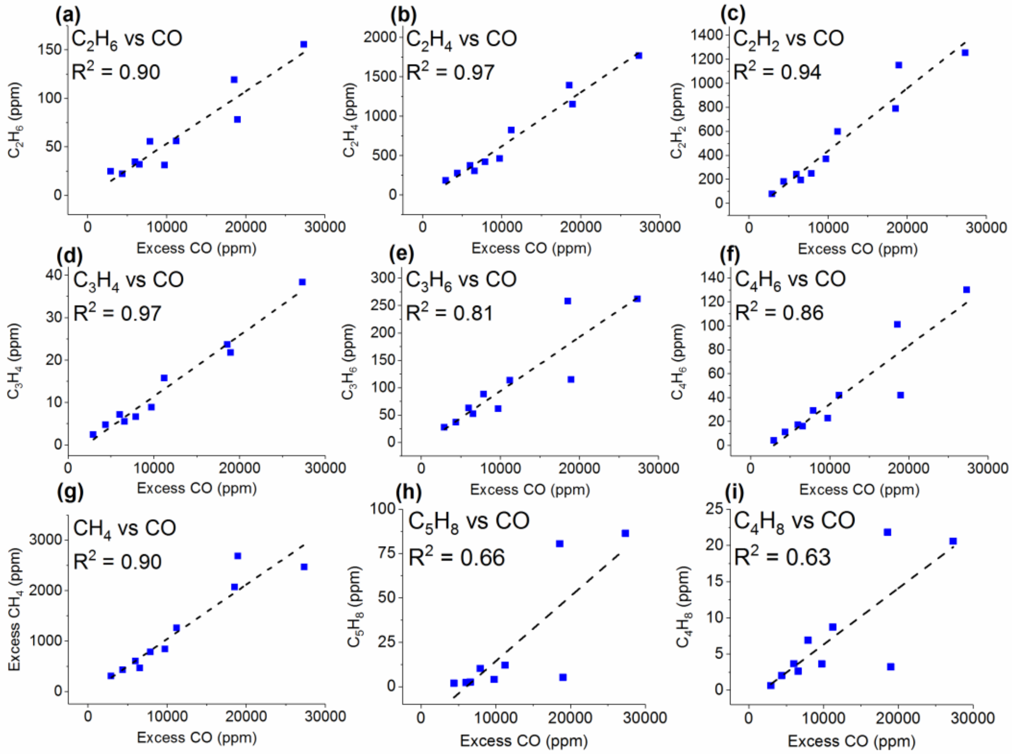

Figure 3. Mixing ratios (ppm) for the 10 measurements as a function of excess CO (ppm) for (a) ethane (C_2H_6), (b) ethene (C_2H_4), (c) acetylene (C_2H_2), (d) allene (C_3H_4), (e) propene (C_3H_6), (f) 1,3-butadiene (C_4H_6), (g) excess methane (CH_4), (h) isoprene (C_5H_8) and (i) isobutene (C_4H_8). The dashed lines are a linear fit to the data.

While the observed emission ratio (ER) for excess methane was comparable, ERs for ethene and acetylene were considerably greater than previously reported values; specifically, Figure 4 shows a comparison for methane, ethene and acetylene to previously reported values of Gilman et al. (2015) and Akagi et al. (2013). As noted, different sampling methods complicate the comparison. The present data represent a collection of instantaneous grab samples extracted directly before the flame front, whereas the other data represent time averaged values. Ethene and acetylene have both been observed as pyrolysis products in prior laboratory work (Palma, 2013), but may react further. For example, the addition reaction of acetylene to benzene or naphthalene can produce styrene or cyclopenta-fused polycyclic aromatic hydrocarbons (PAHs) (Ledesma et al., 2002). Alternatively ethene and acetylene can undergo combustion (Simmie, 2003). Nevertheless, the high ER values for ethene and especially for acetylene in the present study further suggest that the samples were collected when the high temperature pyrolysis process was dominant; Sekimoto et al. (2018) also observed that high temperature pyrolysis profiles are often associated with aliphatic unsaturated hydrocarbons.

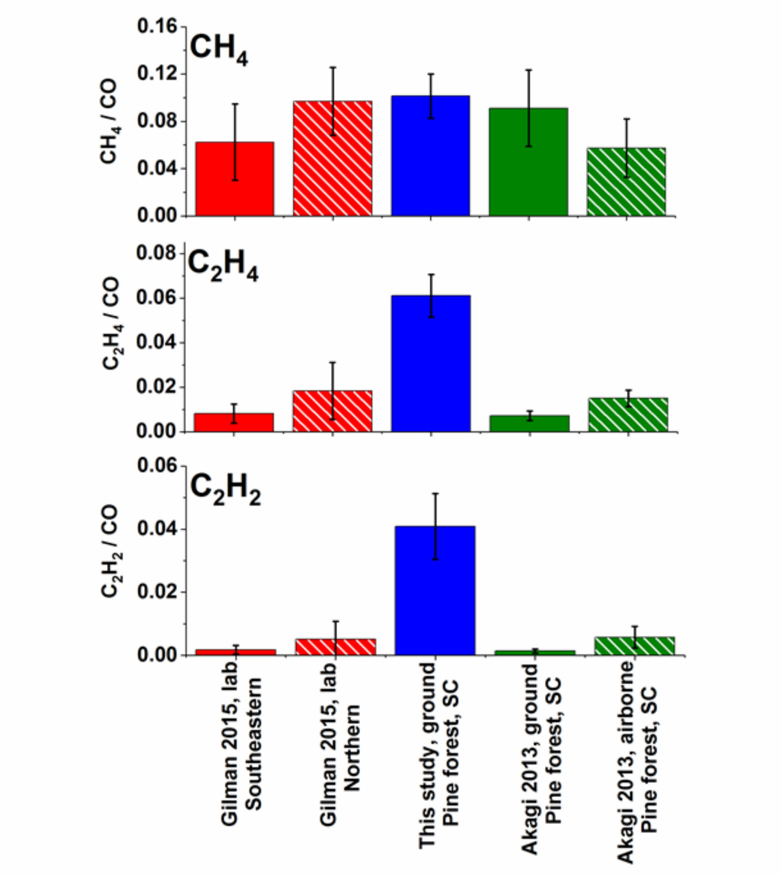

Figure 4. Average emission ratios (ppm/ppm$_{CO}$) for excess methane (top), ethene (middle) and acetylene (bottom) for this study and for previously published laboratory and field (ground and air based) investigations. Error bars represent 1σ. Gilman et al. (2015) present discrete ERs with sample acquisition of 20 to 300 sec. Akagi et al. (2013) present fire-averaged EFs calculated using ERs derived by the regression method. The emission ratios for Akagi et al. shown above were derived from the ratio of the emission factors for the gas of interest and CO multiplied by the molar mass of CO/molar mass of analyte.

3.4 Emissions of Lightweight Oxygenated Hydrocarbons

The noncyclic oxygenated hydrocarbons detected via FTIR analysis include formaldehyde, methanol, formic acid, acetaldehyde, acetone, acetic acid and acrolein. Figure 5 shows average

ERs for these species along with the cyclic compounds furan and furaldehyde. On average, acetaldehyde and methanol had the highest ER values in this group, with ER relative to CO of 0.009 and 0.006, respectively. For all measurements collected at sites 16 and 24A, acetaldehyde was consistently the highest with ER values ranging from 0.005 to 0.014. Site 24B followed a different trend with highest ER values for acetic acid, methanol, acetaldehyde and formaldehyde (in decreasing order). The ERs for acetic acid and formaldehyde at site 24B are at least 7.9 and 2.5 times greater, respectively, than the other burn sites: One key difference for site 24B was fuel composition, namely the presence and partial consumption of larger logs (i.e. 7.6–20.3 cm diameter woody material). Other differences include the presence of live pine seedlings and fewer turkey oak as compared to other plots. This particular plot had the highest herbaceous and forb pre-fire loading and consumption with a higher fuel moisture content (205% as compared to next highest value of 144%). This high fuel moisture content was reflected in the ER for water, which was at least 4.7 times greater than the other plots. The pyrolysis of cellulose (one of the three primary components of biomass as discussed below) forms levoglucosan. Shen et al. (2009) outline secondary decomposition pathways for levoglucosan, in which the initial step is the rehydration to generate glucopyranose. They demonstrate how glucopyranose can then form formaldehyde, methanol and acetic acid via secondary decomposition routes. This pathway (or a similar one) may have been favored at site 24B. The greater ERs for acetic acid and formaldehyde observed at plot 24B may have thus been influenced by the greater fraction of woody material and presence of herbaceous and forb fuels all with higher moisture contents. This hypothesis warrants further investigation.

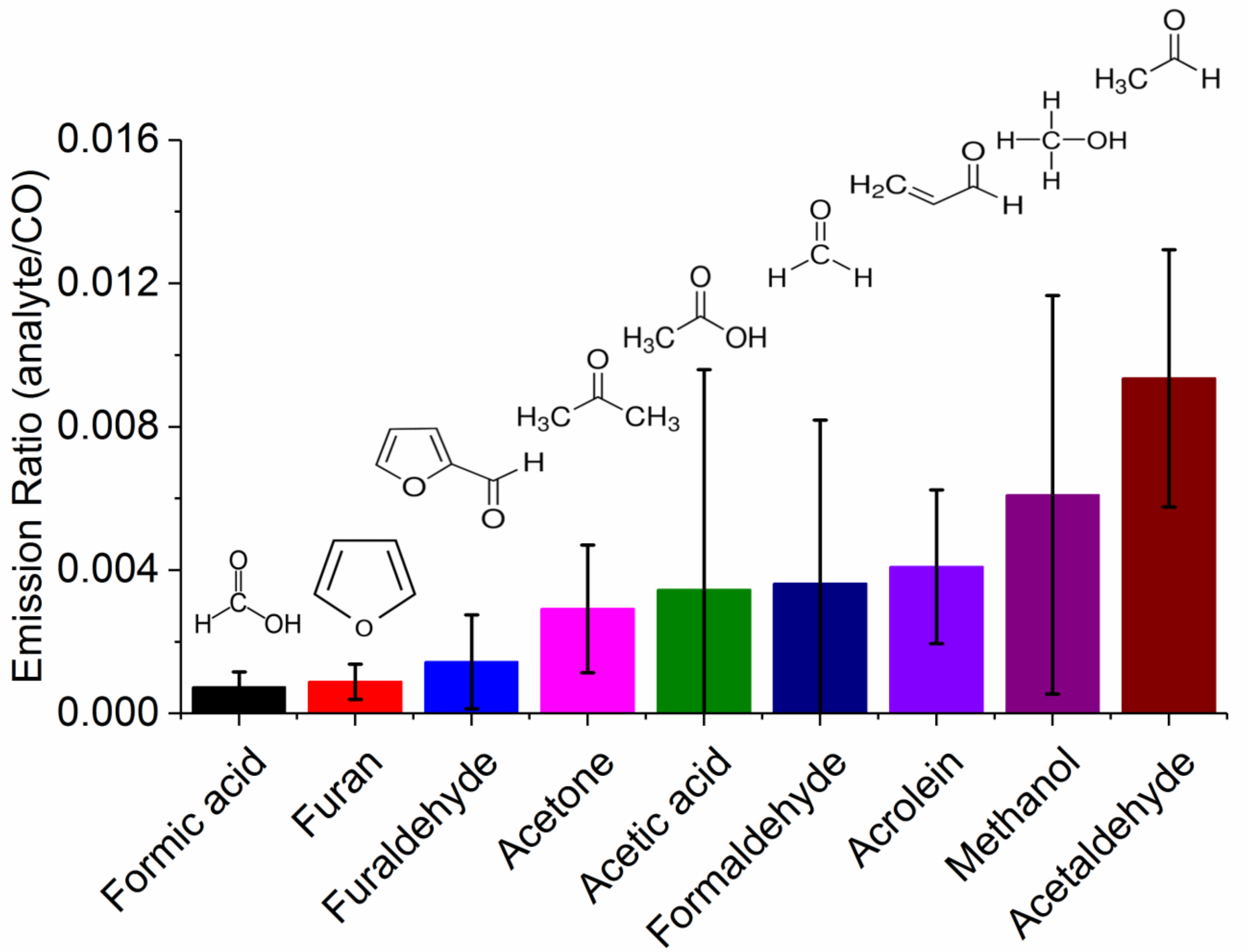

Figure 5. Average emission ratios (ppm/ppm$_{CO}$) for oxygenated hydrocarbons measured by FTIR for the 10 burn samples. Error bars represent 1σ.

Table 3 compares the present ER values with values from Akagi et al. (2013), Stockwell et al. (2014), Gilman et al. (2015) and Koss et al. (2018). The present ERs are comparable to other burn studies except for acetaldehyde, which appears to be marginally greater, and formaldehyde and acetic acid, which both appear to be lower. The higher ratio for acetaldehyde may be due to differences in the sampling approach, i.e. samples collected in the present study may contain species that were generated during an earlier period in the thermal decomposition process. In a controlled laboratory study by Stein et al (1983), acetaldehyde was observed as one of the initial products emitted from the pyrolysis of glycerol, a product pyrolyzed from levoglucosan. This same study also observed that acetaldehyde would continue to decompose (under pyrolysis conditions) to smaller molecules such as ethene, methane, H_2 and CO (Stein et al., 1983). The greater average ER for acetaldehyde observed in the present study may be due to gases being captured (via the collection device) and removed from heat either in-between decomposition steps or before combustion. We note the trend seen in Figure 5 is primarily the lighter alcohols and aldehydes which are the predominant emission species found in these pyrolysis samples, vis-à-vis the aromatics and carboxylic acids. It is possible that the trends seen for the OVOCs in Table 2 and Figure 5, in particular the consistently high values for acetaldehyde may arise due to (a) differing vapor pressures, (b) differing degrees of onset of combustion, (c) differing degrees of pyrolysis emissivity as suggested by Stein et al., (d) differing degrees of sensitivity to IR spectroscopic analysis, or (e) some combination of all these effects. Further analysis is warranted.

Table 3. Average emission ratios (ppb/ppm$_{CO}$) for this study and for previously published fire studies.

Analyte	This Study-Pine forest SC ground-based	Gilman et al., 2015 southeastern Fuels	Koss et al., 2018 study average for all fuels	Stockwell et al., 2014 Sawgrass SC	Stockwell et al., 2014 Ponderosa Pine MT	Akagi et al., 2013 Pine forest SC ground-based	Akagi et al., 2013 Pine forest SC air-based
Formic acid	0.7	1.6	2.2	0.7	5.1	n/a	0.6
Furan	0.9	0.7	1.9	0.8	1.2	2.4	1.1
Furaldehyde	1.5	1.5	2.1	n/a	n/a	0.1	0.2
Acetone	2.9	1.6	2.3	n/a	n/a	3.8	3.6
Formaldehyde	3.6	12	20	7.8	29	12	23
Acetic Acid	3.5	13	n/a	5.2	22	6.6	11
Acrolein	4.1	1.3	5.4	n/a	n/a	1.2	1.8
Methanol	6.1	7.8	12	3.4	24	21	13
Acetaldehyde	9.3	2.8	7.4	n/a	n/a	5.1	4.8

Koss et al. (2018) present the fire-integrated ERs. Gilman et al. (2015) present discrete ERs with sample acquisition of 20 to 300 sec. Stockwell et al. (2014) present the fire-integrated ERs. Akagi et al. (2013) present fire-averaged EFs calculated using ERs derived by the regression method. The emission ratios for Akagi et al. (2013) were obtained from the ratio of the emission factors for the analyte and CO multiplied by the molar mass of CO/molar mass of the analyte.

The slightly lower ERs for formaldehyde and acetic acid may in part be explained by secondary decomposition pathways. Proposed pathways that generate formaldehyde and acetic acid proceed through intermediates formed by the decomposition of levoglucosan (Shen and Gu, 2009). Formaldehyde is generated from a number of intermediates such as hydroxyacetone (acetol) (Lindenmaier et al., 2016) and 5-hydroxymethyl-furfural. While the formation mechanism for acetic acid is via the decomposition of the intermediate hydroxyacetaldehyde (glycolaldehyde) (Johnson et al., 2013), which undergoes a dehydration reaction to a ketene, and then a rehydration to acetic acid (Shen and Gu, 2009), it is possible that the present conditions and fuels (save for site 24B) were not favorable for the above chemical pathways.

3.5 Emissions of Aromatic Compounds

In the present study, furan, furaldehyde and naphthalene were all detected via FTIR. Previous fire studies have used FTIR to detect phenol and/or furan (Burling et al., 2011b; Akagi et al., 2014; Hatch et al., 2017; Christian et al., 2003; Christian et al., 2004; Stockwell et al., 2014b; Karl et al., 2007; Selimovic et al., 2018; Yokelson et al., 2013b; Burling et al., 2010; Akagi et al., 2013). One of these studies also detected furaldehyde (Selimovic et al., 2018). To the best of our knowledge, however, this is the first burning study that has used IR spectroscopy to identify naphthalene vapor, though it has previously been detected in biomass burning emissions via other methods (Koss et al., 2018; Gilman et al., 2015). Naphthalene has also been detected in tar samples generated from the controlled pyrolysis of similar fuels (Safdari et al., 2018).

Phenol and phenolic compounds were not definitively observed in this study due to their IR bands being somewhat weak and obscured by a number of other species, namely acetic acid, carbon dioxide, acetylene and hydrogen cyanide. However, phenolic compounds have been identified in products generated from the pyrolysis of lignin in controlled laboratory experiments by Kibet et al. (2012). Lignin, one of the three main components of biomass, can account for 10–35% of the biomass, and its chemical structure consists of polymers of various phenolic alkyl side chain subunits (Shen et al., 2015). When undergoing thermal decomposition, lignin will release volatiles at temperatures between 200 and 400°C. The proposed mechanism can generate intermediates such as phenoxy radicals that ultimately lead to the formation of phenols (Kibet et al., 2012). In the present study, spectral evidence of phenol was in fact observed in some measurements, but the IR bands at 1176 and 752 $\mathrm{cm^{-1}}$ were weak and were masked by other compound signatures, hindering spectral quantification. Mixing ratios of phenol above the detection limit might have been anticipated since prior controlled pyrolysis investigations of sparkleberry and longleaf pine have detected phenol as a component in the tar (Safdari et al., 2018; Amini et al., 2019a; Safdari et al., 2019). While the phenol signal was weak, furan and furaldehyde, however, were clearly detected, and their formation likely stemmed from thermal degradation of the other main constituents of biomass. Besides lignin, the other primary macromolecular components are cellulose and hemicellulose, which account for approximately 50% and 15–35% by weight, respectively (Shen et al., 2015). The pyrolysis of cellulose is known to produce furaldehyde, furan and other low weight oxygenated compounds (e.g. acetic acid) via the intermediate levoglucosan (Bai et al., 2013). Moreover, furaldehyde and methanol have both been observed as volatile products from the pyrolysis of methyl β-D-xylopyranoside, a model compound for xylan-based hemicellulose (Shafizadeh et al., 1972).

Naphthalene is a polycyclic aromatic hydrocarbon with several sources including a biomass burning emission product. It was detected using FTIR for the first time in these studies(Scharko et al., 2019) . Its IR detection was not unexpected given that it has been observed in collected tar samples generated by the laboratory pyrolysis of similar fuel types (Safdari et al., 2018) but its identification in an experimental IR spectrum can be challenging as seen in Figure 6. Most of its IR bands have only moderate cross-sections with the exception of the ν_{46} band, which has a strong Q-branch at 782.3 cm^{-1} (green trace in Figure 6). For this band to be observed, however, it needs to be deconvoluted from the acetylene rotational-vibrational lines also present in this spectral domain (red trace in Figure 6). Better retrievals for naphthalene were obtained using a higher spectral resolution (0.6 cm^{-1}) since the Q-branch of the ν_{46} band is quite sharp (FWHM ~ 1 cm^{-1}), even at atmospheric pressure (Scharko et al., 2019) .

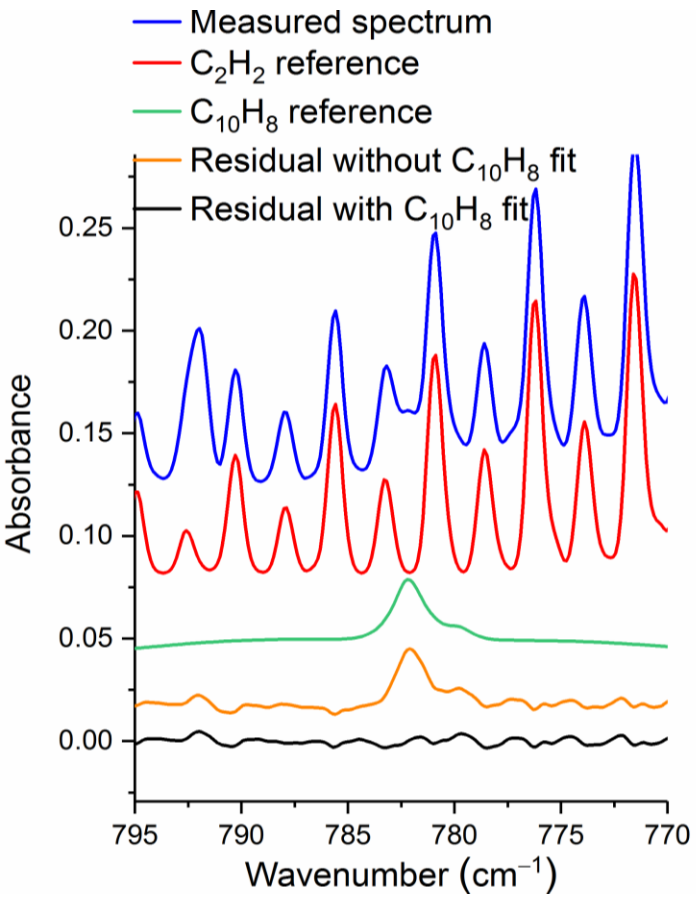

Figure 6. Measured and scaled reference spectra for acetylene (C_2H_2) and naphthalene ($C_{10}H_8$) as well as residual with and without $C_{10}H_8$. The measurement is from site 16 plot 6 msmt. 2, and the detected mixing ratio for naphthalene is 7.37 ppm. Spectra are offset for clarity. Reference absorption lines for acetylene are from HITRAN, and the reference spectrum for naphthalene is from PNNL.

Figure 7a plots the mixing ratios (ppm) for naphthalene as a function of excess CO (ppm) while Figure 7b displays the ERs for naphthalene for this study and previous studies.

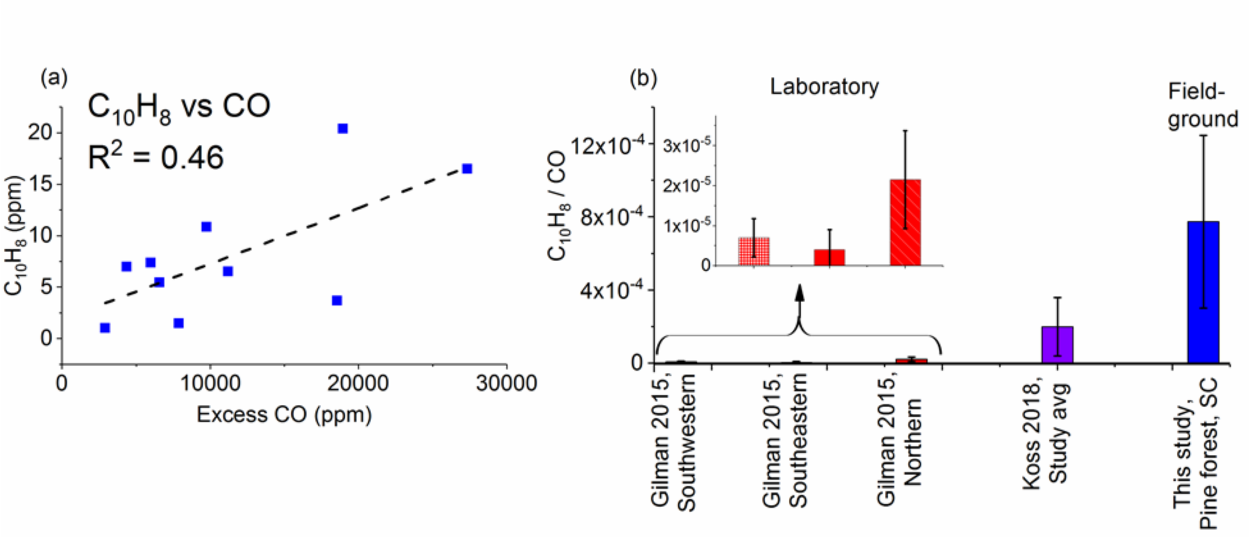

Figure 7. (a) Mixing ratios (ppm) for naphthalene ($C_{10}H_8$) as a function of excess CO (ppm) measured by FTIR for each of the 10 canisters. The dashed line is a linear fit. (b) Average emission ratios (ppm_{C10H8}/ppm_{CO}) for this study and for previous laboratory studies. Error bars represent 1σ. Koss et al. (2018) present the fire-integrated ERs. Gilman et al. (2015) present discrete ERs with sample acquisition of 20 to 300 sec.

The average naphthalene ER for this study is substantially greater than both the values from Gilman et al. (2015) and Koss et al. (2018). The average for Koss et al. (2018), however, is in turn an order of magnitude greater than the highest average for Gilman et al. (2015). The higher ER for naphthalene in this study (shown in Figure 7) clearly suggests that the method to capture pyrolysis gases was (at least in part) quite successful i.e. we were able to collect naphthalene gas prior to it having undergone further reactions. Besides oxidation, under the right conditions naphthalene can also continue to react in a Diels-Alder type reaction to form still larger polyaromatics (Fairburn et al., 1990; Richter and Howard, 2000). Sekimoto et al., (2018) also linked naphthalene with the high temperature profile, and it appears that the samples in the present study were indeed collected when the high temperature process was dominant. The detection of naphthalene suggests that benzene and/or styrene, which are the main precursors to PAHs, may also be present. Styrene was not detected via FTIR methods, and benzene is challenging for IR analysis since its one strong band (ν_{11} mode at 673 cm^{-1}) is obfuscated by the CO_2 ν_2 bending mode under polluted atmospheric conditions.

3.6 Emissions of Nitrogen-containing Species

Gases such as NH_3, NO_2, NO, HCN and HONO have been identified using FTIR spectroscopy in fire laboratory experiments multiple times (Selimovic et al., 2018; Gilman et al., 2015; Christian et al., 2003; Christian et al., 2004; Goode et al., 1999; Yokelson et al., 1996; Yokelson et al., 1997; Stockwell et al., 2014b; Hatch et al., 2017; Burling et al., 2010; Karl et al., 2007) as well as in field studies (Yokelson et al., 1999; Burling et al., 2011b; Goode et al., 2000; Akagi et al., 2013; Karl et al., 2007; Akagi et al., 2014). Multiple other methods have also been used to detect N-containing gases, such as HNCO and CH_3CN (Gilman et al., 2015; Christian et al., 2003; Christian et al., 2004; Yokelson et al., 2009; Akagi et al., 2013; Karl et al., 2007; Roberts et al., 2010). The amount and speciation of N-containing compounds emitted is dependent on fuel type and nitrogen content (Stockwell et al., 2014b; Burling et al., 2010; Coggon et al., 2016). Moreover, emissions can usually be linked to a stage of combustion: NO, NO_2, HNCO and HONO are all associated with the flaming stage, while NH_3 and HCN are primarily associated with smoldering combustion but have also been suggested as pyrolysis gases (Goode et al., 1999; Yokelson et al., 1996; Roberts et al., 2010; Burling et al., 2010; Hansson et al., 2004; Di Blasi, 2008). Biomass pyrolysis experiments carried out in an inert (i.e. oxygen free) atmosphere have revealed that NH_3, HCN and HNCO are all generated (Hansson et al., 2004). These compounds are all considered to be NO_x ($NO + NO_2$) and N_2O precursors because they are oxidized via combustion (Hansson et al., 2004).

It is important to note that N-bearing compounds, amines in particular, are often best sampled via open-path techniques such as an open White Cell, as these compounds are notorious for adhering to walls of sampling of analysis devices, including those made from steel, glass or Teflon (Stockwell et al., 2014a; Yokelson et al., 2003). Sampling and passivation techniques have been discussed extensively (Neuman et al., 1999; Roscioli et al., 2015) for these “sticky” molecules, and the present method may thus not be optimal for these compounds. Nevertheless, the major N-containing compound identified in the present pyrolysis study was HCN. This is consistent with previous small-scale and controlled laboratory studies that have shown HCN as the primary N-product resulting from the pyrolysis of amino acids (Haidar et al., 1981; Johnson and Kan, 1971). This observation is further evidence that the gas samples were extracted when high temperature was the dominant process; Sekimoto et al., (2018) have associated HCN with the high temperature pyrolysis profile. Figure 8a shows the correlation between HCN and excess CO (R^2 = 0.89). Previous field fire studies have observed similar trends (Simpson et al., 2011; Stockwell et al., 2016). Figure 8b shows a comparison between the ERs for HCN for this study as well as from previous laboratory and field (both ground and airborne) studies. The present values are comparable to other ground-based measurements (Guérette et al., 2018; Akagi et al., 2013) but differ from a few of the laboratory and airborne-based studies. It should be noted that although conducted at a different time of the year (late Oct./early Nov. 2011), the studies by Akagi et al. (2013) took place near the same location as the current study (i.e. the same military base), and the ERs for HCN between the studies are not significantly different for the ground-based measurements. This suggests that the ratio of initial gases released of HCN to CO is consistent with the ratio of these gases over the duration of the fire, or at least the fire-averaged ratio. With regards to ERs for HCN, the major factor that appears to influence these values is fuel type, particularly the fuel's peat content. Both laboratory (Stockwell et al., 2014b) and field (Stockwell et al., 2016) studies of Indonesian peat have shown greatly enhanced ERs for HCN compared to the studies represented in Figure 8b, which consist mostly of pine, grasses and fuels of non-peat origin. The range in the averages of ERs for HCN shown in Figure 8b is 0.0028–0.0095; the averages for the Indonesian peat in laboratory and field studies were 0.015 and 0.021, respectively (Stockwell et al., 2014b; Stockwell et al., 2016), and interestingly are ~an order of magnitude greater than the range of values seen in Figure 8b.

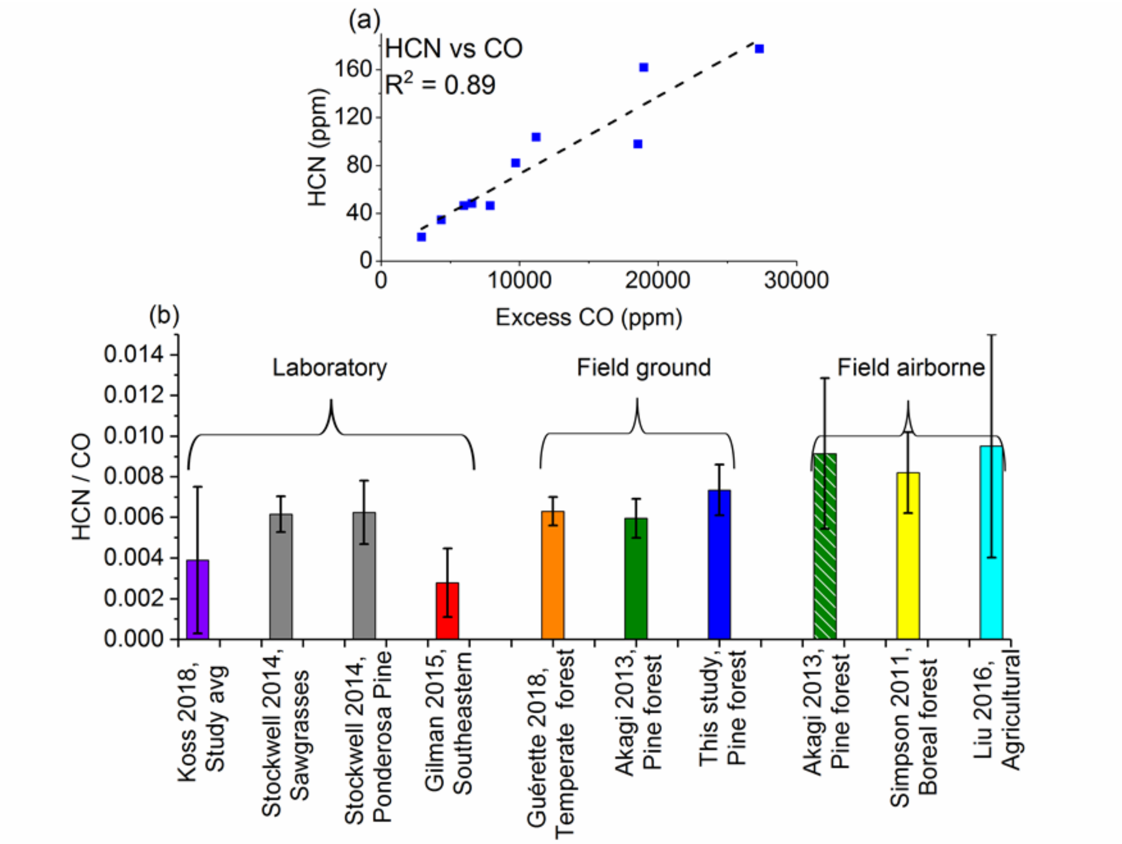

Figure 8. (a) Mixing ratios (ppm) for HCN as a function of excess CO (ppm) measured by FTIR. The dashed line is a linear fit. (b) Average emission ratios (ppm/ppm CO) for this study and previous laboratory and field investigations. Error bars represent 1σ. Koss et al. (2018) and Stockwell et al. (2014) present fire-integrated ERs. Gilman et al. (2015) present discrete ERs with sample acquisition of 20–300 s. Simpson et al. (2011) present fire-averaged ERs derived by regression. Guérette et al. (2018) present a single ER from all fires and derived by regression. Akagi et al. (2013) and Liu et al. (2016) present fire-averaged EFs calculated using ERs derived by regression. The ERs for Akagi et al. (2013) and Liu et al (2016) were derived from the ratio of the EFs for HCN and CO multiplied by the molar mass CO/molar mass HCN.

In the present study, trace amounts of HONO were detected, but NH_3 was not observed. The absence of NH_3 was somewhat unexpected since, similar to HCN, it is a known product from the pyrolysis of amino acids (Haidar et al., 1981) and has been observed in prior prescribed fires conducted at Ft. Jackson (Akagi et al., 2014; Akagi et al., 2013). There are several possible explanations for the lack of NH_3 in the measurements. First and foremost, experimentally NH_3 is well known to adhere to certain surfaces (e.g. steel), and in this study it may have adhered to the canisters or tubing walls and was thus not detected (Neuman et al., 1999; Roscioli et al., 2015; Stockwell et al., 2014a; Yokelson et al., 2003). Second, Sekimoto et al., (2018) observed that NH_3 is associated more with a low temperature pyrolysis profile, and it appears that the present samples were extracted during a period when high temperature pyrolysis was the main process. Third, NH_3 is strongly linked with the smoldering phase (Goode et al., 1999; Yokelson et al., 1996), and samples were not collected during this phase. Fourth, the speciation of the N-species emitted is dependent on the fuel composition and amount of oxygen (Ren and Zhao, 2013a, b, 2012), so it is possible that in the present study, the conditions favored HCN instead of NH_3.

The IR quantification of other N-species, such as NO, NO_2, CH_3NO_2 and HNCO was obstructed due to interferences from H_2O, CO and CO_2 as well as the low emission values for some of these N-species. Since NO and NO_2 are usually associated with flaming combustion, it was not unexpected that these species were not observed. HNCO has been linked with pyrolysis processes, and its main formation pathway is the cracking of cyclic amides along with HCN which is also a product of pyrolysis, Hansson et al. (2004).

After accounting for the challenges in measuring NO, NO_2 and HNCO, the second most prevalent N-containing species observed in this work was methyl nitrite (CH_3ONO). Methyl nitrite has previously been detected in emissions from biomass burning using other methods (Gilman et al., 2015). Figure 9a shows the plot of mixing ratios for methyl nitrite as a function of excess CO. Unlike HCN (Figure 8a), methyl nitrite exhibits minimal correlation with excess CO. As one possible alternative explanation, methyl nitrite is known to be associated with rocket-propelled grenades (RPGs), but the Ft. Jackson military base records did not indicate RPG usage for these burn plots(Scharko et al., 2019). While few fire studies have observed methyl nitrite, Gilman et al. (2015) have detected it using GC-MS. Figure 9b shows a comparison of the results from Gilman et al. (2015), separated by U.S. region, with the present results. It is worthy to note that both studies observed similar ERs and that in the Gilman study, methyl nitrite had the second highest mean ER after HCN for N-bearing species in southwestern fuels. Our observation of methyl nitrite is thus not unprecedented, but this was its first reported detection via FTIR(Scharko et al., 2019) . In the present study, three measurements (Site 16, plot 1, msmt 1; Plot 24A, msmt 3; and Plot 24B) had higher ERs for methyl nitrite than the others, and it is unclear why this is the case. Other measurements collected at the same location reported lower ER values. If the three highest ER measurements in question are not included in the regression then the correlation between methyl nitrite and CO is stronger, and the average ER is closer to values reported by Gilman et al. (2015) for southeastern fuels. One possible explanation for the three greater ER values is that the fuels may have contained more components such as nitrate esters and isopropyl nitrate, both of which are known to release minor amounts of methyl nitrite under controlled pyrolysis conditions (Boschan et al., 1955; Griffiths et al., 1975).

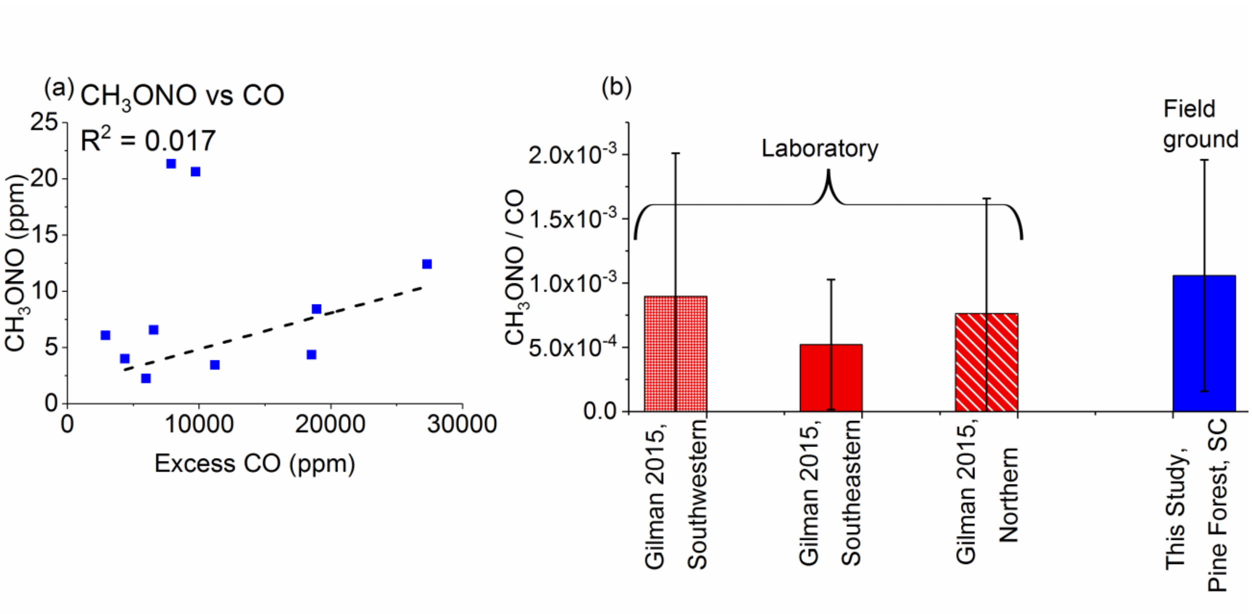

Figure 9. (a) Mixing ratios (ppm) for methyl nitrite (CH_3ONO) as a function of excess CO (ppm) as measured by FTIR. The dashed line is a linear fit. (b) Average emission ratios (ppm/ppm CO) for this study and previously published study carried out in the laboratory. Error bars represent 1σ. Gilman et al. (2015) present discrete ERs with sample acquisition of 20 to 300 s.

4. CONCLUSIONS

The objective of this study was to collect and quantify gas-phase compounds emitted ahead of the flame front (prior to the onset of combustion) in prescribed burns conducted in a pine forest. Primary and secondary decomposition pathways generate volatile products, which act as fuel gases that can undergo combustion and contribute to sustaining the fire. The main observations are that the estimated ratio of high to low temperature VOC emissions suggest that the samples were indeed extracted when the high temperature pyrolysis process was dominant. The acetylene/furan ratio suggested by Sekimoto (2018) was nearly 10x higher than previous studies; this is in fact consistent as previous works all had longer collection times, in some cases fire-averaged values. The significantly greater ERs observed for specific compounds, e.g. lightweight HCs such as ethene and acetylene as well as unoxidized aromatics such as naphthalene all support the hypothesis that the grab samples were collected prior to onset of decomposition, recombination or combustion reactions, and that such gases represent pyrolytic processes. For the oxidized organics, acetaldehyde and methanol consistently had the highest ER values relative to CO for this collection of pyrolysis gases. The ERs for acetic acid and formaldehyde were found to be high in some instances, but this appeared to be related to fuel composition of the individual burn site. The major N-component released was HCN, while NH_3 was not observed, which is consistent with the collected gases representing species associated with the high temperature pyrolysis process, but collection of NH_3 and amines is always problematic due to adhesion. It would be interesting to study the effects of initial pyrolysis gas composition ratios on the composition of the downwind plume (Johnson et al., 2006; Johnson et al., 2009).

ASSOCIATED CONTENT

Author contribution

NKS, TLM, and TJJ contributed to the writing of this manuscript. AMO and RGT set up laboratory and recorded infrared data. NKS, AMO and CAB provided data processing and analysis. SPB, ENL, JC, BMC and GMB aided in collection of field samples. JC provided thermal imaging and videography. RDO and JRC contributed to fuel characterization. DRW and TJJ were the project managers.

Supporting Information

The Supporting Information is available free of charge.

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