Our responses are interspersed with the reviewers' comments and are given in red italic text. The line numbers where those changes appear in the revised paper are also given at that point. The revised main text and supplemental information are posted as additional author comments.

Anonymous Referee #1
General comments:
The authors present an overview of the N-budget during the FIREX campaign, bringing together datasets from a variety of instruments and techniques (outlines in Table 1) in already peer-reviewed articles of FIREX work. This analysis is certainly a great contribution to the field and specifically to the science of reactive nitrogen budgets from forest fires. The methods used are state-of-the-art, including the instrumentation used for acquiring the data during the campaign in addition to the data analysis, including PMF. I command the authors on putting this data set together and anticipate this contribution, upon revision, to be a go-to paper for the atmospheric organic-N and inorganic-N fate from biomass burning, well fitting within the scope of Atmos. Chem. Phys.
We thank the reviewer for their kind words and hope that our revisions will meet with approval.

My most significant revision recommendation is related to the writing and to the presentation of the research. It is difficult to read the manuscript as the information is presented in no specific order and without pertinent subsections. Lots of information is relayed, but it is unclear what the scientists set out to do in the first place. My specific feedback is below to improve the manuscrupt.
We have revised the manuscript to better organize and emphasize the various subsections. Specific changes involved dividing the Results Discussion section into subsections and adding introductory sentences describing the specific research question to be answered. Never-the-less, we do believe the information is presented in the correct order, as the Results section proceeds from the most general (total N_r and total carbon) to the most specific (factors that define emissions composition). We hope that the division into sub-sections, with the addition of introductory material will make that more apparent. We think the last sentence of the Introduction adequately explains what we set out to do in the first place "The results are used to arrive at suggested guidelines that can be used estimate N_r-emissions profiles for fires representative of western North America."

Scientific feedback:
It is unclear to me exactly what the conclusion of the work is. Is it that N mass balance was achieved in this study (stated in lines 298-299 – which seems to be a particularly important finding in my opinion, even one to be highlighted as the title, or at least feature predominantly in the abstract)? Is that N_r can/cannot be predicted (mentioned on lines 337-338)? Is it that the dominant molecules of N_r were identified? Is it that an estimated N_r/C ratio of 0.37% can be recommended for modeling (lines 450-452)?
Yes, the reviewer has correctly listed most of the major findings of this work. We would add that we show how the composition of N_r has a systematic dependence on the temperature of combustion/reaction in answer to the reviewers' question RE lines 337-338. We have added a sentence about the N/C ratio to the abstract to better emphasize that conclusion. We have also reformulated the budget statement in the abstract to say that measured individual N_r species accounted for 84.8 (±9.8)% of the measured N_r on average. We point out that all of these findings appear in the section labeled "Conclusions". Never-the-less, we have taken steps to better emphasize them as we have reorganized the paper as outlined below.

It seems like the authors touch upon each one of these questions but the support for these conclusions can be better communicated. In my opinion, they are all important questions for the field which this paper nicely addresses, but currently in a rather disordered fashion. My advice is to use subsections addressing each one of the scientific questions listed (and others as the authors see fit) and present the data in a logical way: (1) state the hypothesis and research question; (2) show the appropriate figure and state the results; (3) discuss the implications of the work.

We thank the reviewer for their advice. We have reorganized the paper, including more subsections and expository statements to guide the reader, as the reviewer has suggested. Specifics changes are shown in red in the Revised paper.

The Comb-N, HT-N and LT-N factors represent different classes of N_r emissions during biomass burning. What was the big picture goal here? Was it to know that for example when NH_3 is detected in a plume, that temperatures related to LT-N are taking place at the origin for the fire? In other words, are these identified chemical markers used to estimate the temperature and burning stage of the fire? If so, then the authors should add this goal to their abstract, highlight this result in their conclusion and devote a titled sub-section to this analysis.

The big-picture goal here was to look for relationships between the detailed N emissions that we measured and simple measures or marker compounds that could serve as a means to estimate emissions when detailed measurements were not available. We started with MCE, because of the extensive history that MCE has with the wildfire emissions community, and found that MCE does not correlate (either positively or negatively) with an important fraction of N_r. As a result, we used PMF to find that three factors were much better able to describe WF emissions and their variation corresponded to roughly three temperature regimes. These temperature regimes made sense in relation to what we know about combustion and pyrolysis chemistry. We then could select several chemical markers to help in representing these combustion regimes. We have now added emphasis to the abstract and the re-organization of the Results and Discussion section provides the sub-sections requested by the reviewer. We have further emphasized this result in the Conclusions.

Which research question was being addressed by comparing chaparral fuels within this study? Is the information distracting from the other main messages? Is it necessary to include the analysis related to the chaparral fuels in this paper?

The intent of this phase of the FIREX project was to study emissions from fuels characteristic of Western North American Wildfires. Chaparral ecosystems are important throughout Central and Southern California and other areas of the Southwestern U.S. Thus, we feel the research on chaparral fuels belongs in this paper. We mention the importance of chaparral fuels in the paper on Lines 142-143.

Why place an emphasis on Batch 1 and Batch 2 (including Table 2) if the conclusions are that the same factors were obtained irrespective of which "Bacth was used" (explained in lines 367-368)? Is it necessary to describe both of these PMF analysis? I would argue (although happy to be convinced otherwise) that this description is not necessary for the analysis presented in this manuscript. Only one batch could be described (would also affect Table 2) and a simple one-sentence mention that the same factors were obtained with and without inclusion of CO2, CO and Nr.

We agree and have now changed the discussion to note the results were the same when including CO, CO_2 and N_r, and present only the runs previously denoted 'Batch 2" in Table 2 and results. Lines 237-240.

I'm curious to know whether there is a "time" component expected for the Nr budget. In other words, would the Nr species evolve over time away from a plume of biomass burning? If so, how? There is mention of flame chemistry on lines 348-362 and Figure 8 (where there is a clear behavior of multiple generation production). For example, the brown carbon properties of biomass burning aerosols respond to heterogeneous oxidation (see (Browne et al., 2019)). For example, are the organic-nitrogen compounds evolving from amines to amides to isocyanates (see (Borduas et al., 2016))?

A goal of this work was to investigate how combustion partitioned fuel N. In these experiments in the Firelab the emissions undergo essentially no further processing once they leave the flame /smoldering zone. So, no there is not a "time" component to the N_r budget in the sense that the reviewer means, i.e. based on the quoted references. As a result, discussion of these aspects of processing is not appropriate *for this paper, which focusses on emissions. Yes, there is a whole rich body of work on BB atmospheric processing, some of which was done as part of this FIREX FireLab study, but it does not apply to our topic.*

HNO3 is mentioned in the text (lines 87; 94-98; 300-301) but it wasn't clear where its discussion fits within the topic of Nr. Could the authors specify the significance and consider adding a subsection on HNO3?

$HNO_{3(g)}$ would be easily measured by the N_r and OP-FTIR technique if it was present, and therefore needs to be mentioned. What we perhaps did not make clear is that HNO_3 is not observed above detection limit (10 ppbv). This was due to the large particle surface area loading and the high NH_3 present, both favoring immediate conversion of any $HNO_{3(g)}$ to particle nitrate, essentially by the time the smoke reached the top of the stack (5 sec). This does not warrant another section, instead we have now made this clearer in the text and in the discussion: Lines 161-163, and Table 1.

Lines 281-289: Is the goal of this section to update MCE values with this work, or to compare the MCE values to the literature? Which values are to be used in further modelling for instance?

The whole fire MCE values are summarized in Selimovic et al., 2018. The goal of this section of our paper is to contrast our findings on fuel N conversion to N_2 and N_2O with previous measurements and estimates in the literature. Since high temperature combustion conditions and associated flame chemistry are required for this conversion, we use this opportunity to place our observations in the context of the previous studies by using MCE as the key indicator of this combustion chemistry. We do not use MCE in any modeling as we later show, it does not capture the dependence of emissions on temperature.

I'm curious about the atmospheric implications of yak dung (lines 307-310).

Yak dung is an important domestic fuel in a number of developing countries, especially in ecosystems above timberline or where wood is scarce. These emissions can impact outdoor air chemistry in areas such as India, Nepal, and Tibet, (see Xiao et al., 2015 for example). In addition, Yak dung emissions have not been measured by a suite of instruments as extensive as those used in this work, and represent something of an extreme case of a high nitrogen/carbon fuel that typically burns at lower MCEs. Lines 143-144.

Based on the results from FIREX, would the authors continue to recommend acetonitrile (line 311) as an adequate biomass burning tracer?

In many cases, acetonitrile is a very good tracer of biomass burning, but Coggon et al., (2016) noted that solvent sources of acetonitrile can sometimes obscure the BB signature, and that acetonitrile is sometimes quite low in emissions from heartwood that is often burned in woodstoves. HCN is a more reliable signature for the HT-N pyrolysis stage of WF emissions and it is also high in peat and dung fires so can serve as a good tracer for those too. We have now noted this in lines 477-480.

Lines 322-323: HNCO and HCN are organic compounds (of which the definition is any molecule which contain at least one carbon and one hydrogen) and shouldn't be included in the "inorganic N" category and discussion.

This is a very interesting area of discussion and could take up a lot of time if we tried to cover it in this paper. By the Reviewer's definition, sodium bicarbonate ($NaHCO_3$) and carbonic acid (H_2CO_3) would be considered organic compounds, but the vast majority of scientists would disagree with that. More complete definitions specify that an organic compound contains carbon, hydrogen, and perhaps oxygen, nitrogen and sulfur, ***covalently bound****. This is the key to classifying HNCO and HCN, as these H-C and H-N bonds are ionic, not covalent: both compounds are weak acids, and dissociate in aqueous solution.*

Presentation feedback:

The best way to improve the manuscript is by structuring the text. The results are interesting but are buried in paragraphs with a lack of order. Every paragraph could have subsections identifying the main message of the results.

In general, the structure of a paragraph starts with a topic sentence about what the paragraph will describe. I think being attentive to that structure could really help bring flow to this manuscript. (For example, one could also avoid starting paragraphs by pointing to a Figure (lines 271-272)).
As described above, we now have divided the Results and Discussion section into more subsections, with the addition of introductory sentences where needed, so that we are not starting sub-sections by pointing to a Figure. We note that occasionally it makes sense to start paragraphs within a sub-section by introducing a new or contrasting figure that is part of the larger topic of that sub-section.

The scientific research questions could be better identified and articulated. For example, the abstract starts with stating the method, without giving context, the research question and the hypothesis. A short revision here could help the reader situate the study.
We have added sentences to the beginning of the abstract to accomplish this.

Lines 84-87 cites a long list of references. I would argue that this list is not so useful unless each study is briefly described and the main message is communicated.
We have now provided a brief description for those papers on Lines 91-97.

Lines 164-166: would be great to show this data (in the suppl info).
A discussion of the effect of diffusion and dispersion due to laminar flow is now included in the SI, along with comparison of the NO and N_r signals to those of the OP-FTIR, that show the effective 4 sec time constant. And we note that in Lines 186-187

Lines 208-211: could give an example of the calculation
We now give an example calculation at this point. Line 231-232.

Table 1 is a great summary of the techniques and compounds included in this study. However, I was a little confused about the meaning of the "references" column. The references from where the data from FIREX was published should be identified separately. I think there are currently 5 publications from FIREX which this study correctly references. What is the meaning of the references prior to 2016? Are they instrument references? It would be great to add further details here as well as provide all the acronyms of the instruments in the caption.
The 'References' column is now relabeled 'Method Reference' to make it clear that these are the publications that described the methods. As a result, several pre-date this lab study. We have spelled out the acronyms, as requested.

Figure 1: The equations aren't mass/atom balanced. For example, HCN → O, OH → CN is a misleading representation of the reaction. One can use curve arrows to show the intermediates with their own products. Or one can add all the products next to the specie. The chemical equations should be mass balances in any case. In addition, it would also be useful to denote all radical species (either with a dot or another way). I would avoid the (s) notation at it is typically reserved for the solid phase. Perhaps H_2O + surface could be clearer.
Indeed, there are reactions presented here that are not balanced. The purpose of presenting this material in Figure form is to make it easy to see the general flow of the chemistry with a rough separation by temperature regime. A more thorough representation of the chemistry with the various mechanisms and products would unnecessarily clutter a diagram like Figure 1. What the reviewer seems to be asking for is an exhaustive listing of balanced equations, which is really beyond the goals of this paper, and in fact is

very ably covered by Glarborg et al., (2018). We have added more details across the bottom of the diagram, so for example $CN + O_2 \rightarrow NCO + O$ *now form a balanced equation. We have added dots to denote radical species as requested. We now use* $H_2O_{(surf)}$ *to denote surface-adsorbed water.*
We note that Reviewer 2 liked Figure 1, and requested only a few additions as noted below.
We have added a sentence to clarify the intent of Figure 1, (Lines 75-77).

Lines 386-396: an important message! So temperature is a better predictor than MCE? Interesting!
The word "predictor" is difficult because we don't have a measure of the actual fire temperature. We prefer to think of it as the N_r *speciation correlating with temperature as indicated by key chemical species, and yes, we feel this is one of the key conclusions of the work.*

Technical comments:

Lines 37-43: This sentence is 7 lines long and could be broken down into 3-4 sentences.
We have removed a redundant clause and changed the last clause into a sentence.

Line 44: define chaparral fuels
We have specified manzanita and chamise on Line 48.

Line 76: use arrow instead of "=>"
Done, and an arrow was also added to the chemical equation that was on line 77. Lines 83-84.

Lines 115-123: best to use the present tense in this paragraph rather than future tense (which reads more a like a proposal).
By convention, the last paragraph in an Introduction describes what the paper will present, rather what has already been done in the area of research being addressed. As a result, phrasing this paragraph in the future tense could help to make this apparent. However, we acknowledge the use of present tense is common and we have changed to the present tense since both reviewers appeared to take issue with this approach.

Line 256: Is the "emitted carbon" in the gas phase or the particle phase?
It is both, which seems clear from the sentence "The additional carbon species included methane and a number of other gas phase VOCs as well as organic- and black-carbon aerosol."

Figure 3: the x-axis in 103 ppmv-sec was a little misleading. Took me a few minutes to understand/see that there was a factor of 1000 between the y-axis and the x-axis. Could be worth highlighting these units differently.
We now highlight the different in scales in the figure caption. We think this, and the fact that the figure has lines ranging from 0.25% to 2% drawn on it should make the scale difference clear.

Figure 10: top panel is arguably redundant and could be removed. (same for the equivalent figure in the suppl. Infor)
We disagree. The top panels in these figures show different information from the bottom panels of these figures. The top panels show the fraction of each factor that is accounted for by each of the compounds or subclasses, while the bottom panel shows how the compounds or subclasses are distributed among the three factors, so by nature, each compound or class in Figure 10b adds up to 1.0. Take for example the subclass 'nitro-compounds', Figure 10b shows how it is divided among the three factors, but Figure 10a shows that it is a relatively small contributor to any one factor. There is no way to get that information from Figure 10b. These features of Figure 10 were clearly stated in the text (Lines 431-433). Note that Figure 10 in the original is now Figure 9.

Table 3: Could be better represented as a graph?

We have considered this and wish to keep this as a Table. The reason being that many current models are not equipped to use the temperature-dependent emissions information we are presenting, but can include simple representations of N emissions. In those cases, these tabular data are most convenient.

References:

Borduas, N., Abbatt, J. P. D., Murphy, J. G., So, S. and da Silva, G.: Gas-Phase Mechanisms of the Reactions of Reduced Organic Nitrogen Compounds with OH Radicals, Environ. Sci. Technol., 50(21), 11723–11734, doi:10.1021/acs.est.6b03797, 2016.

Browne, E. C., Zhang, X., Franklin, J. P., Ridley, K. J., Kirchstetter, T. W., Wilson, K.R., Cappa, C. D. and Kroll, J. H.: Effect of heterogeneous oxidative aging on light absorption by biomass burning organic aerosol, Aerosol Sci. Technol., 53(6), 663–674, doi:10.1080/02786826.2019.1599321, 2019.

Anonymous Referee #2

The paper presents a unique and high quality set of observations of reactive nitrogen from smoke emanating from laboratory burns of predominantly western U.S. fuels. Variability in the emissions of specific reactive nitrogen species are modeled using a positive matrix factorization (PMF), and the paper makes recommendations on specific markers to be used for emissions of reactive nitrogen emissions from combustion, high-temperature pyrolysis and low-temperature pyrolysis. The overall content is already largely suitable for publication in ACP, but some improvements to the structure could make it much easier to digest. Thus most of my comments are editorial in nature.

Edits:

Line 135: It seems like particle phase measurements were made during the FIREX burns? I immediately wondered… Why is there no use of the LTOFAMS data to compare to the "particle-bound" species that are "not included in this analysis"?

The particle measurements at the top of the stack were limited to the optical measurements described by Selimovic et al. (2018), particle organic species measurements described by Jen et al., (2019), and a Compact Time-of-Flight Aerosol Mass Spectrometer (C-ToF-AMS). The CToF-AMS had only unit-mass resolution and because of that, and large deviations from typical mass fragmentation patterns, could not give quantitative measures of ammonium or inorganic nitrate. There were HiResToF and LToF-AMS instruments used for the chamber experiments associated with the FIREX-Firelab project but the aerosol was often manipulated in novel ways to better understand aerosol properties, and processing, and that precluded measuring emission factors. Hence, while they were able to look at process chemistry, they did not sample direct emissions.

Section 2.3 PMF Analysis: The methods/details in this section really do need to be expanded so that this analysis is actually reproducible. Please add Q/Qexp values, FPEAK values, and the number of bootstrapping runs for all calculations.

We have now described those in Sections 3.5 and 3.7, and we have added information on our original PMF of Fire 063 in the SI that shows the robustness of the analysis for Fpeak =-1, 0, and +1, and bootstrapping runs with 100 different seeds. Lines 423-427.

This section would substantially benefit from some better organization. I had to read many of the paragraphs twice to make sure I understood them and I often felt like the order was random. I recommend looking through this section and dividing it into several new more specific sub-sections, rather than just

one sub-section (i.e. current 3.1). Perhaps it would be better to have non-western U.S. fuels (e.g. the Yak Dung) just appear in the SI, rather than in the main text. This might help Section 3 feel more focused.
We have reorganized this section substantially due to both this Reviewers' and Reviewer #1's comments. This reorganization involved dividing Section 3 into a number of smaller subsections, and moving the original Figure 6 (yak dung) to the SI.

Comments Specific to Figures:

Figure 1: This is really nice. Could you add a list (or denote in some way – that would be even better) all the species not measured in this study?
We now note that species measured in this work are shown in bold and slightly larger font, and the species not measured are shown in normal text.

I think there is value in having Figure 2 in the main text. It is nice because it shows the evolution of the fire, and how the reactive nitrogen and carbon-containing species evolve as a result. However, the use of Figure 5 and Figure 6 feels tedious. The text is sufficiently wordy that the reader has to go into those time series and try to interpret/summarize the patterns themselves. I would recommend that there is only one time series Figure and then the others are moved to the SI. If there is something specific to see in Figure 5 and Figure 6 that is contrasting between the fires or called out in the text, then those sections of the plots should be highlighted somehow, maybe with transparent yellow bars.
We have now moved Figure 6 into the SI. We wish to retain Figure 5 because it shows a number of things the Figure 2 does not, specifically the details of the N_r *composition, and that Residual* N_r *evolved with time during the fire. That the Residual* N_r *is relatively higher at the end of the fire when smoldering emissions are more prevalent, is now shown with a yellow box in Figure 5.*

Figure 3: Why is Duff twice without noting differences between them?
We have now labeled the different types of duff on Figure 3b.

Figure 11: I would combine the top two panels of Figure 11. Why show a R2 of a linear fit in panel d) when that relationship is not linear?
We have now combined the top two panels into one that shows, CO_2*, MCE, and Comb-N Factor. The* R^2 *for (now) panel (c) is given as a means to quantify the deviation of the relationship from linear. Please note that Figure 11 in the original is now Figure 10.*

Minor Edits:

Line 97: Combine parentheses around citations.
Done.

Lines 115 – 123: This paragraph should be in present tense, not future. The jump to future tense here is disorienting.
Changed as noted above.

Line 168: change "into" to "by"
Done.

References:

Coggon, M., Veres, P. R., Yuan, B., Koss, A. R., Warneke, C., Gilman, J. B., Lerner, B., Peischl, J., Aikin, K., Stockwell, C. E., Hatch, L. E., Ryerson, T. B., Roberts, J. M., Yokelson, R. J., and de Gouw, J.: Emissions of nitrogen-containing organic compounds from the burning of herbaceous and arboraceous *biomass: fuel composition dependence and the variability of commonly used nitrile tracers, Geophys. Res. Lett., 43, 9903-9912, 2016.*

Jen, C. N., Hatch, L. E., Selimovic, V., Yokelson, R. J., Weber, R., Fernandez, A. E., Kreisberg, N. M., Barsanti, K. C., and Goldstein, A. H.: Speciated and total emission factors of particulate organics from burning western US wildland fuels and their dependence on combustion efficiency, Atmos. Chem. Phys., 19, 1013-1026, 2019.

Selimovic, V., Yokelson, R. J., Warneke, C., Roberts, J. M., deGouw, J. A., Reardon, J., and Griffith, D. W. T.: Aerosol optical properties and trace gas emissions by PAX and OP-FTIR for laboratory-simulated western US wildfires during FIREX, Atmos. Chem. Phys., 18, 2929-2948, 2018.

Xiao, Q., Saikawa, E., Yokelson, R. J., Chen, P., Li, C., and Kang, S.: Indoor air pollution from burning yak dung as a household fuel in Tibet, Atmos. Environ., 102, 406-412, 2015.

The nitrogen budget of laboratory-simulated western U.S. wildfires during the FIREX 2016 FireLab study

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Abstract. Reactive nitrogen (N_r, defined as all nitrogen-containing compounds except for N_2 and N_2O) is one of the most important classes of compounds emitted from wildfire, as N_r impacts both atmospheric oxidation processes and particle formation chemistry. In addition, several N_r compounds can contribute to health impacts from wildfires. Understanding the impacts of wildfire on the atmosphere requires a thorough description of N_r emissions. Total reactive nitrogen was measured by catalytic conversion to NO and detection by NO-O_3 chemiluminescence together with individual N_r species during a series of laboratory fires of fuels characteristic of Western U.S. wildfires, conducted as part of the FIREX FireLab 2016 study. Data from 75 stack fires were analyzed to examine the systematics of nitrogen emissions. The measured N_r/total-carbon ratios averaged 0.37% for fuels characteristic of western North America and these gas phase emissions were compared with fuel and residue N/C ratios and mass to estimate that a mean (±std. dev.) of 0.68 (±0.14) of fuel nitrogen was emitted as N_2 and N_2O. The N_r detected as speciated individual compounds included: nitric oxide (NO), nitrogen dioxide (NO_2), nitrous acid (HONO), isocyanic acid (HNCO), hydrogen cyanide (HCN), ammonia (NH_3), and 44 nitrogen-containing volatile organic compounds (NVOCs). The sum of these measured individual N_r compounds averaged 84.8 (±9.8)% relative to the total N_r, and much of the 15.2% "unaccounted" N_r is expected to be particle-bound species, not included in this analysis.

A number of key species, e.g. HNCO, HCN and HONO, were confirmed not to correlate only with flaming or only with smoldering combustion when using modified combustion efficiency (MCE = CO_2/(CO + CO_2)) as a rough indicator. However, the systematic variations of the abundance of these species relative to other nitrogen-containing species were successfully modeled using positive matrix factorization (PMF). Three distinct factors were found for the emissions from combined coniferous fuels~~, aligning with our understanding of combustion chemistry in different temperature ranges~~: a combustion factor (Comb-N) (800-1200°C) with emissions of the inorganic compounds NO, NO_2 and HONO, and a minor contribution from organic nitro compounds (R-NO_2); a high-

temperature pyrolysis factor (HT-N) (500-800°C) with emissions of HNCO, HCN and nitriles; and a low-temperature pyrolysis factor (LT-N) (<500°C) with mostly ammonia, and NVOCs. The temperature ranges specified are based on known combustion and pyrolysis chemistry considerations. The mix of emissions in the PMF factors from chaparral fuels (manzanita and chamise) had a slightly different composition: the Comb-N factor was also mostly NO, with small amounts of HNCO, HONO and NH_3, the HT-N factor was dominated by NO_2 and had HONO, HCN, and HNCO, and the LT-N factor was mostly NH_3 with a slight amount of NO contributing. In both cases, the Comb-N factor correlated best with CO_2 emission, while the HT-N factors from coniferous fuels correlated closely with the high temperature VOC factors recently reported by Sekimoto et al., (2018) and the LT-N had some correspondence to the LT-VOC factors. As a consequence, CO_2 is recommended as a marker for combustion N_r emissions, HCN is recommended as a marker for HT-N emissions and the family NH_3/particle ammonium is recommended as a marker for LT-N emissions.

1 Introduction

Wildfires have severe impacts on the chemistry of the atmosphere from local to global scales (Crutzen and Andreae, 1990). A warmer, drier climate in western North America, coupled with policies that have allowed build-up of fuels in forest ecosystems has led to increases in frequency and severity of wildfires in this region (Abatzoglou and Williams, 2016; Westerling et al., 2006). The new strategy for management of wildfire in the U.S. is to allow fire where possible and to fight fire where needed (Lee et al., 2014). The science behind making these decisions and understanding their consequences involves, in part, a better understanding of the emissions from wildfires. The NOAA FIREX (Fire Influence on Regional and Global Environments Experiment) FireLab experiment was conducted in the Fall of 2016, at the U.S. Forest Service Fire Sciences Laboratory in Missoula, Montana, to acquire detailed measurements of particle and gas-phase emissions from fires involving fuels characteristic of the western U.S. (NOAA, 2018). Several aspects of these measurements dealing with VOC species, and individual reactive nitrogen species (N_r, defined as all nitrogen compounds except for N_2 and N_2O) have already been published (Koss et al., 2018; Manfred et al., 2018; Sekimoto et al., 2018; Selimovic et al., 2018; Zarzana et al., 2018), including emissions factors for many of the N_r-species (Koss et al., 2018).

The N_r compounds emitted by natural-convection biomass burning (BB) arise solely from the N in the fuels, since the combustion temperatures are not high enough (<1200°C) to produce oxides of nitrogen (NOx) from N_2 and O_2 (the so-called Zeldovich or thermal nitrogen cycle) (Lobert and Warnatz, 1993; Taylor et al., 2004; Wotton et al., 2012). The fuel nitrogen cycles that pertain to BB flaming combustion are shown schematically in Figure 1 (Glarborg et al., 2018; Lobert and Warnatz, 1993; Lucassen et al., 2012; Manion et al., 2015). Note that the equations shown in Figure 1 are meant to indicate the general flow of the chemistry and do not always convey the mechanistic subtleties of the reactions, which are fully covered in specialized references (Glarborg et al., 2018; Manion et al., 2015). N_r compounds are emitted as small molecules, hydrogen cyanide (HCN), isocyanic acid (HNCO), and ammonia (NH_3) resulting from pyrolysis of the fuel, with minor contributions from larger N-containing organic species, especially at lower temperatures. Flame chemistry converts those species to N_2, N_2O, nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous acid (HONO) as a result of radical chemistry. It has been recognized for some time that a significant amount of denitrification (conversion of N_r compounds to N_2) occurs due to reactions of NO with NH_i (where i= 1, 2, or 3) or N atoms, as confirmed experimentally (Kuhlbusch et al., 1991). While N atoms are also intermediates in the thermal NO_x cycle and the reaction $N + O_2 \rightarrow NO + O$ figures in to both the fuel and thermal NO_x cycles, the second reaction of the thermal NO_x cycle, $O + N_2 \rightarrow NO + N$, is too slow at BB flame temperatures to result in NO_x production (Manion et al., 2015). In addition to the small molecules shown in Figure 1, numerous N_r-compounds are emitted in roughly the following categories: amides, amines, heterocyclic compounds, nitriles, isocyanates, and nitro compounds (Andreae, 2019; Andreae and Merlet, 2001; Koss et al., 2018; Lobert et al., 1991; Lobert et al., 1990; Lobert and Warnatz, 1993; Stockwell et al., 2015). These compounds are produced at much lower abundance from fuel pyrolysis and partial reactions with the radical species in Figure 1.

The emissions of N-compounds from BB and wildfires in general have been the subject of considerable research. Early studies by Lobert et al., (1990, 1991, 1993) measured a wide range of N_r compounds in laboratory fires and suggested that considerable denitrification (conversion of fuel nitrogen to N_2) was taking place, a process later confirmed in experiments described by Kuhlbusch et al., (1991). Subsequent work on laboratory fires has better defined particle phase nitrogen emissions (McMeeking et al., 2009) and led to the recognition of the importance of several inorganic N_r species, such as HONO and HNCO (Burling et al., 2010; Roberts et al., 2011; Veres et al., 2010), and the presence of a wider variety of organic N_r species (Gilman et al., 2015; Stockwell et al., 2015; Warneke et al., 2011). A number of studies have sought to summarize both real world and laboratory emissions of N_r compounds (Akagi et al., 2011; Andreae, 2019; Andreae and Merlet, 2001; Coggon et al., 2016; Yokelson et al., 2013b; Yokelson et al., 2009). The known N-compounds range in oxidation state from NH_3 to HNO_3 and include N_2 and N_2O. Among the more prominent and important N_r species are: NO_x (NO and NO_2) which is a key player in the atmospheric oxidant cycle; NH_3 which has a major role in particle formation; ~~nitrous acid (~~HONO~~)~~ which can be an important radical source; HCN and acetonitrile (CH_3CN) which are toxic at high concentrations and represent valuable tracers for following fire transport; and isocyanates, HNCO and methyl isocyanate (CH_3NCO) which have unique health impacts (Roberts et al., 2011). In addition, nitro ($-NO_2$), or nitrogen heterocyclic compounds may contribute to so-called brown carbon, aerosol organic compounds exhibiting optical absorption in the near-UV or blue wavelength regions. Wildfire N emissions also have very minor contributions from gas phase nitric acid (HNO_3). Nitric acid is either not efficiently produced by BB or is readily incorporated into aerosol if it is produced in fresh wildfire plumes, as is clear from the absence of HNO_3 enhancements in several studies of BB plumes (Liu et al., 2016; Yokelson et al., 2009)Alvarado et al., 2010), however nitrate (NO_3^-) has been shown to contribute to aerosol mass particularly for inefficient combustion (May et al., 2014). Flame chemistry is inefficient in forming N_2O, relative to the pathways that form N_2 (Andreae, 2019; Andreae and Merlet, 2001; Griffith et al., 1991; Hao et al., 1991). The modeling of the emissions of these N-compounds on a large scale could benefit from a better understanding of the total budget of these species as a function of fuel nitrogen content and the dependence of the individual species on fuel type and combustion conditions.

The construction of N_r-budgets in this work is made possible by the inclusion of a total reactive nitrogen measurement (termed N_r herein), a method by which all nitrogen compounds besides N_2 and N_2O are converted to NO and detected by NO-O_3 chemiluminescence. This technology has been developed by a number of groups, typically using precious metal or NiCr catalysts that have been shown to convert all N_r compounds to NO (and to some extent

NO_2) at high temperatures (750-825°C) (Hardy and Knarr, 1982; Kashihira et al., 1982; Marx et al., 2012; Roberts et al., 1988). There are also commercial instruments that incorporate this technology (see for example Thermo Scientific Model 17i). This technique has been applied to gas phase atmospheric measurements, principally to measure NH_3 by difference techniques (Saylor et al., 2010; Schwab et al., 2007), and has also been used to observe wildfire plumes that have impacted ambient air measurements (Benedict et al., 2017; Prenni et al., 2014). We have recently developed a platinum/molybdenum oxide N_r catalyst system, and confirmed that it quantitatively converts N_r compounds including all particle-bound nitrogen compounds (Stockwell et al., 2018). To our knowledge this technique has not been applied directly to BB emissions before.

This paper ~~will~~ describes the total reactive nitrogen, and individual N_r compound measurements made during the FireLab 2016 experiment, with the intent of providing information that can be used for analysis and modeling of the impact of wildfire emissions on the atmosphere. The total N_r measurements ~~will be~~ are combined with CO_2, CO, and VOC measurements and fuel, residue and ash C and N content to estimate the amount of N lost to N_2 and N_2O. In addition systematics of the ratio Nr/Total Carbon are examined for simplifying relationships. Fire-integrated N_r ~~will be~~ is then compared to fire-integrated measurements of individual compounds to determine the fraction of unaccounted-for N_r. The systematic behavior of individual N_r species and their fractional contribution to N_r ~~will be~~ are examined with respect to fuel type, N content, and combustion processes. A positive matrix factorization (PMF) technique ~~will be~~ is used to examine commonalities between fires of different fuels under different conditions and compared to the PMF analysis of the VOC emissions published by Sekimoto et al., (2018). The results ~~will be~~ are used to arrive at suggested guidelines that can be used estimate N_r-emissions profiles for fires representative of western North America.

2 Methodology

The FireLab 2016 study involved laboratory burns of fuels mostly characteristic of western North American wildfires such as coniferous fuels and chaparral fuels (important in central to southern California and the southwestern U.S.). We also measured some that have global significance such as Indonesian peat and yak dung (important in areas above timberline or where wood is scarce, such as India, Nepal, and Tibet). The procedures and associated details of the study have been described previously by Selimovic et al., (2018) and will be only briefly summarized here. The detailed data on fuel types, amounts and composition can be found in Table S1, and in the Supplemental section of Selimovic, et al., (2018). The laboratory burns involved fuel samples, ranging in mass from 0.26 to 6.02 kg spread out on a fuel bed roughly 1m x1m square. Fires were started without the addition of any contaminants, using an electric igniter (a series of NiCr heating elements that were flash-heated electrically), and typically lasted from approximately 5 to 30 minutes. Seventy-five fires were conducted in the "stack" burn configuration where the smoke was directed up the central stack of the facility where it could be sampled simultaneously by all the instruments that measured gas phase species, and some of the particle phase measurements. The sampling platform was about 15 m above the fire and the sampling took place in well-mixed smoke approximately 5s after emission (Christian et al., 2004). Thirty-one additional fires were conducted as "room" burns on most of the same fuels, when the stack was closed and the room was allowed to fill with smoke, permitting sampling to be done over the course of several hours. The following analyses will focus on the "stack" burns, as those measurements had little or no interferences from surfaces, where "room" burns are known to be compromised by the loss of materials, such as NH_3, to the room walls at long sample times (Stockwell et al., 2014). Ash analyses were performed only on the residues from the room burns and those values will be used for the N and C budget calculations, with the assumption that stack and room burns left similar ash considering the combustion conditions were the same for each type of fire. Table 1 lists the compounds and associated techniques used to measure them during the FireLab 2016 study, and describes the grouping of NVOCs measured by PTR-ToF into common categories, e.g. amines, nitriles, etc. We specifically note that the OP-FTIR is capable of measuring gas phase HNO_3 with comparatively good sensitivity (10ppbv detection limit in fires where N_r can be 5 ppmv or more), but HNO_3 was not observed above detection limit in any of the fires.

2.1 N_r and NO measurements by Chemiluminescence

Total reactive N (N_r) was measured by catalytic conversion to NO, followed by O_3-chemiluminescence using an instrument described previously (Williams et al., 1998). N_r and NO were sampled from inlets inserted adjacent to the inlet-less open-path Fourier transform infrared spectrometer (OP-FTIR) instrument path during the stack burns (Selimovic et al., 2018), and from a platform approximately 4 m off the floor in the middle of the room during the room burns. The catalyst used for the N_r channel, described in detail by Stockwell et al. (2018), consisted of a 11mm I.D. quartz tube, packed with 36 platinum screens, heated to 750°C. This tube was wrapped with high temperature heating tape and insulated inside a 7cm OD stainless steel tube that was fitted to a bulkhead placed through the wall of the stack. The N_r channel was diluted by a factor of 5:1 (±3%) using a flow of zero air added immediately downstream of the Pt catalyst assembly. NO was sampled through a 6.3mm O.D. stainless steel inlet tube which was placed through the bulkhead directly into the free air stream of the stack and connected to a 50mm Teflon filter holder immediately outside the stack. The transfer lines for the N_r and NO measurements consisted of 6.35mm O.D, 1mm wall thickness PFA tubing of approximately 20 m in length. N_r and NO data were acquired at 1 s frequency, but the flow rate through each inlet was 1 SL min^{-1}, resulting in residence time in each inlet of 14 s. This time delay was corrected in the data analysis. Any chemical effects of the inlet on the sampled air stream were negligible since the analytes consisted of only NO and NO_2 and those are known to be transmitted by PFA Teflon tubing with essentially no surface effects. However, there were possible effects of the inlets on the temporal features of the measurement through diffusion or turbulent mixing. Those effects were examined through comparison of the temporal variations in the NO signal with the NO measured by the OP-FTIR, and comparison of the N_r signal under smoldering conditions with the NH_3 measured by the OP-FTIR. Both of these comparisons showed that the NO and N_r inlets had effective time constants of 4 seconds, somewhat slower than the diffusive relaxation time assuming solely laminar flow. Examples of the estimate of diffusion and dispersion on NO and N_r signals, and the estimate of the effective time constant of these measurements are presented in the Supplemental Information.

The inlet streams were sampled by the NO instrument either directly (NO channel) or after passing through a second catalyst of molybdenum oxide (MoOx) to convert remaining NO_2 to NO. The MoOx catalyst consisted of a molybdenum tube at 350°C to which a small flow of H_2 (0.8%v/v) was added to control the re-dox state of the surface. Both channels of the instrument were "de-tuned" to keep raw photon count rates below 4 MHz, by turning down the

O_3 flows and PMT voltages. Calibrations were performed with both a NO standard in N_2 (Scott-Marrin) and 10.1 ppmv standard of HCN in nitrogen (Gasco). The Pt catalyst was dismounted from the stack (or room) every few days and checked for conversion efficiency by the addition of the HCN standard to the inlet. Conversion efficiencies were found to be consistently high (>98%) throughout the entire sampling period (October 5 – November 12, 2016). There were slight background signals (a few tens of ppbv) for both NO and N_r in both the stack and room air prior to and after the burns, and those were subtracted from the fires signals prior to reporting the data. The overall uncertainties in the NO and N_r data were ±10% for each measurement.

2.2 Other measurements

Measurements of individual species during the 2016 FireLab study have been presented in several previous publications. The OP-FTIR measurements were discussed by Selimovic et al., 2018, and the PTR-ToF measurements were discussed by Koss et al., (2018). In addition, some of the calibration methods and GC separation and identifications rely on additional analytical work presented by Sekimoto et al., (2017) and Gilman et al., (2015). We measured the mass and elemental content of the initial fuel and the mass of unburned fuel for all the fires, and we measured the mass and the elemental content of the ash during 21 room burns, which covered all the fuel types discussed.

2.3 PMF Analysis

Trace gas measurements from multiple instruments involved in the FireLab study were combined and analyzed using positive matrix factorization (PMF). PMF is a numerical method that was used in this case to partition the compounds involved in a time varying mixture of chemicals into a few groups, or “factors”, where a compound can appear in more than one factor. A factor represents a consistent profile of compounds that is representative of one of the sources contributing to the total signal. The sum of all the “factors” then ideally describes the total composition of the measurements, which in this case is the emissions of N_r compounds. By its nature, PMF assumes that the total signal is a linear combination of individual sources that have a consistent composition, the relative contribution of which is represented by the amount of each compound or category found in each factor (Paatero and Tapper, 1994; Ulbrich et al., 2009). We hypothesize that species with dominant fractions in the same factor are related to each other via the same formation processes. With knowledge of factor composition and the amount of each factor at any given time the original emissions measurements can be reconstructed and this approach provides an alternate source of profiles for fire emissions. PMF has also been used by a number of groups to explore how much various source profiles contribute to complex ambient measurements (see for example Ulbrich et al., 2009) and was recently used to analyze PTR-ToF-MS measurements from the FireLab (Sekimoto et al., 2018). Here, PMF was accomplished using the PMF Evaluation Tool v. 2.08A (Ulbrich et al., 2009).

The application of PMF to this data set is different than the instances where it is applied to data from a single instrument in which compound abundances are inherently scaled properly and error estimates are well defined and self-consistent. For example, when applied to mass spectral data from a single instrument, errors can be expected to scale as the square root of ion counts based on fundamental counting statistics (Sekimoto et al., 2018). In this work we are including nitrogen measurements from several instruments, thus we chose to use mixing ratios as the unit of comparison. The error estimates required by the PMF analysis were taken from the reported combined uncertainties: the sum of the detection limit plus the estimated random error of the measured value. For example, the uncertainty in a NO mixing ratio of 500ppbv was ±51ppbv. The variables that were used in this PMF analysis and their units and corresponding errors are listed in Table 2. Where compound categories are specified (e.g. nitriles), the values were the sum of the measured compounds in that category as listed in the footnotes to Table 1. The data were further adjusted by subtracting the ambient air background before and after the fires, which was a relatively minor adjustment for most compounds and categories. Any negative numbers that resulted were very small compared to the fire emissions, and were set to zero. In addition to the PMF analysis for the species listed in Table 2, several exploratory runs were tried with CO_2, CO added (in units of ppmv) and total N_r (in units of ppbv) added to the list in Table 2. No significant differences were observed in the results for individual N_r compounds and classes, so CO_2, CO and Total N_r were not included in this analysis.

~~Two approaches were taken when performing PMF analyses. The first approach included all individual N-containing compounds together with CO_2, CO, and N_r in the analysis batch (Batch 1), while the second excluded the latter three species (Batch 2). CO_2 and CO were included because of their well-known roles as indicators of flaming and smoldering combustion, respectively, an effect traditionally captured through the use of Modified Combustion Efficiency (MCE) defined as~~

~~MCE = $\Delta CO_2/(\Delta CO_2 + \Delta CO)$ (Eq. 1)~~

~~where ΔCO_2 and ΔCO are the CO_2 and CO levels above the ambient. When CO_2 and CO were included, the carbon species were put into the PMF in units of ppmv, and all the nitrogen species in units of ppbv. This was done because the nitrogen levels were on the order of a percent or less compared to the carbon species. The second analysis batch (Batch 2) involved only the individually-measured nitrogen species and categories listed in Table 1 so that factor loadings would be reflective of the nitrogen-only emissions. Batch 2 factors indicate how N_r species are related to each other via combustion chemistry.~~

We applied PMF to single fire data as well as extended time series that included all fires of a particular fuel type, in-line with the approach laid out by Sekimoto et al., 2018. By consolidating fuels from a particular vegetation type, the fire to fire variability largely driven by differences in the fuel (e.g. moisture content, structure, quantity) is constrained and the most representative fire conditions are captured. Two fuel groups were analyzed in this way: the western U.S. coniferous ecosystem fuels which included ponderosa pine, lodgepole pine, Douglas fir, Engelmann spruce, and sub-alpine fir and the Southwestern U.S. chaparral ecosystem which was represented by chamise and manzanita. The consolidated time series for the coniferous ecosystems included realistic mixtures, canopy only, and litter only, while duff and rotten logs were analyzed separately, and not included in the timeseries.

3 Results and Discussion

The measurements of total N_r can be combined with N and C measurements of fuel and ash to estimate N lost to N_2 and N_2O. The total N_r emitted from laboratory fires combined with individual N compound measurements allow us to construct a budget for N_r species that define what the dominant forms of N are and how those emissions depend on other fire parameters, or different temperature combustion processes. The systematics of N emissions found by PMF are compared to other fire indicators and PMF analyses previously conducted on VOCs allow the formulation of simplifying relationships that can be used in atmospheric models of wildfires.

3.1 Comparison of N_r and Total Carbon in fire emissions

The total N_r and total carbon emissions were measured for 75 stack fires in order to place the N emissions in the context of total carbon which has be widely estimated for wildfires. Example timeseries of NO, N_r, ΔCO, ΔCO_2 (CO and CO_2 corrected for their backgrounds) are shown in Figure 2, for a fire burning a sample of ponderosa pine realistic mix (Fire 004). In addition to the chemical species, the modified combustion efficiency (MCE) was also plotted. MCE is defined as

$$MCE = \Delta CO_2/(\Delta CO_2 + \Delta CO) \qquad \text{(Eq. 1)}$$

where ΔCO_2 and ΔCO are the CO_2 and CO levels above the ambient. MCE has traditionally been used to indicate the relative amount of flaming and smoldering combustion in a fire. The timeseries for Fire 004 (Figure 2) shows a short initial smoldering/distillation phase (MCE 0.7 to 0.8) as heat pyrolyzes the fresh fuel and releases VOCs from existing pools in the fuel followed after ignition by a relatively efficient mix of flaming and smoldering combustion (MCE 0.95 to 0.98) and then finally a subsequent period of essentially pure smoldering (MCE ~0.80). The N_r and NO timelines had many features in common because NO is often the most abundant N_r compound (see below). As a result, it is useful to compare the quantities N_r–NO and $(N_r\text{-NO})/N_r$ to the other measures of chemical species or combustion efficiency. As expected, $(N_r\text{-NO})/N_r$, in Figure 2(c) is anti-correlated with MCE since N_r is primarily NO at high MCE. In addition to the anti-correlation, this non-NO fraction, like its approximate carbon analog CO/CO_2, has a wider dynamic range than MCE and will often suffer less from background variability than carbon-based indices (Yokelson et al., 2013a).

The concentration profiles of the background-corrected measurements of N_r, CO_2, CO, and all the carbon-containing species measured by the FTIR (Selimovic et al., 2018) during the stack burns were integrated over the entire time of the burn to obtain total carbon, termed TC here, and total N_r. The additional carbon species included methane and a number of other gas phase VOCs as well as organic- and black-carbon aerosol. Altogether these carbon species should account for ≥98% of emitted carbon (McMeeking et al., 2009). Total N_r is plotted in Figure 3, versus TC (Figure 3a) and versus nitrogen burned, which is calculated from the %N in the fuel × the mass of fuel consumed (Figure 3b). The points in Figure 3 are colored by the fuel N/C mole % obtained from the elemental analysis of each fuel. The relationship between N_r and TC in panel 3a clusters around the 0.37% line and those points are from fuels most characteristic of the North American biomes impacted by wildfire. There are clear outliers in the correlation of N_r and TC; for example, yak dung and two samples of duff (Engelmann spruce and subalpine fir) were high due either to the fact that they have high fuel N/C ratios (dung, see Table S1), or they burned with minimal flaming (whole fire MCEs 0.86-0.89, duff and dung), hence experienced less de-nitrification. The fuels that were low in N_r/TC in panel 3a, ponderosa pine rotten log, subalpine fir and excelsior, had low fuel N/C, so when plotted versus nitrogen burned in panel 3b, they cluster with the main group of characteristic fuels, i.e. they are no longer 'outliers' in the distribution.

3.2 Estimates of denitrification

The removal of N to forms in-active in the troposphere, N_2 and N_2O, has importance in the biogeochemistry of forest ecosystems and also determines how much N takes part in wildfire plume chemistry. The points in Figure 3a are all lower than the corresponding fuel N/C mole ratio, due to the denitrification chemistry, shown in Figure 1, and verified in lab studies described by Kuhlbusch et al. (1991), and the production of N_2O which is also not measured by the N_r technique. The sum of N_2 and N_2O produced in the fires can be estimated from the difference between the fuel N/C and the N_r/Total C emitted and the data on C and N content remaining in the ash. The mass balance equations used for these calculations are detailed in the Supplemental Materials.

The distribution of the N lost to N_2 and N_2O is shown in Figure 4. Chemical analyses were not done for all fuels during the stack burns, and the analysis above assumes that the ash residues and ash/burned fuel ratios from the stack burns were well represented by those for the same fuels used in the room burns, for which mass yields and chemical analyses were done. Data are missing for fuels that did not have a corresponding residue analysis. The median fraction of N lost to N_2 and N_2O for ash-corrected fires was 0.70, and the mean (±standard deviation) was 0.68 (±0.14). This fuel-based estimate is uncertain by approximately 25% because of the above assumptions concerning the applicability of the residue analyses from the room burns and because fuel moisture corrections were assumed to apply to all of the materials burned, foliage vs. woody biomass (see SI for details). The emission of N_2O relative to N_2 is approximately 10% or less for a wide range of fuels (Andreae, 2019). Assuming the N remainder in our work is at least 90% N_2 gives values that are somewhat higher than the N_2 values reported by Kuhlbusch et al., (1991) where N_2 accounted for 36% of fuel N burned in flaming stage fires. A closer inspection of Kuhlbusch et al., (1991) showed a range of N_2 yields of 40-54% at highest MCEs of 0.94-0.97. Possible reasons for these differences are that the Kuhlbusch et al., (1991) fires were limited to grasses, hay, and pine needles, and the fires were confined to a closed container and so may not have experienced the convection and turbulence of typical biomass fires. In addition, the fires analyzed in our work were somewhat weighted towards the full canopy and higher temperature burning fuels, since ash analyses were not done for peat, dung and many of the "litter" samples, all of which tend to burn less efficiently. Goode et al., (1999) estimated an N_2 emission of 45±5% for MCE values of 0.95 in grass and surface fuels. The range of values determined in our work overlap with these literature values, but are on average higher. It should be noted that such loss of reactive nitrogen can have implications for ecosystem N budgets, as discussed by Kuhlbusch et al., (1991).

3.3 The budget of N_r and individual N containing species

The composition of the N that does not get converted to N_2 or N_2O is of intense importance in determining atmospheric impacts of fires, since those compounds are involved in oxidation capacity (NOx), radical production (HONO) and particle formation (NH_3). Emission factors for all the individual N_r compounds identified in our work have been compiled and reported in previous publications (Koss et al., 2018; Selimovic et al., 2018), so this paper will focus on the N_r budget. The balance of N_r budget for Fire 047, sub-alpine fir realistic mix, is shown in Figure 5, in which the timelines of N_r, NO, N_r-NO, sumN, and NVOC are plotted along with MCE and (N_r-NO)/N_r. The quantity sumN is the sum of all other non-NO compounds, and NVOC is the subset of sumN that are organic nitrogen compounds measured by the PTR-ToF, as listed in Table 1. This fire had a mixture of flaming and smoldering combustion throughout the fire as indicated by MCE and nitrogen profiles (panel (d)). The comparison of N_r-NO with the sumN in panel (b) shows that much of the N is accounted for. The major contributors to sumN for this fire were HNCO, HCN, HONO, NO_2, and NH_3, while NVOC was a very small contributor to sumN (panel (b)). Note that while HNO_3 is measurable by FTIR with good sensitivity, no HNO_3 signals were observed above detection limit, which was 10 ppbv. Panel (c) shows the residual left after NO and sumN are subtracted from N_r, corresponding to an integrated amount of 15.6 ±8% of N_r. This residual is reasonable considering typical published particle N_r measurements (Akagi et al., 2012; Akagi et al., 2011; Liu et al., 2017; May et al., 2014), and consistent with there being some particle N_r from flaming, which are most likely organic nitrates or nitro-organics, and particle ammonium from smoldering with potassium or ammonium nitrate potentially accounting for substantial N_r.

Several fuels had much lower NO emissions and higher unaccounted for N_r. Yak dung was one such fuel the emissions of which stand in contrast to the fire shown above. The nitrogen emissions from Fire 050, yak dung, are shown in Figure S2. This fuel produced mostly smoldering emissions as exemplified by the low NO levels relative to N_r (panel a), and the low MCEs observed (panel d). The sum of N_r species was somewhat correlated with the quantity N_r-NO, but was substantially lower, and the residual N_r unaccounted for by the gas-phase measurements was 33.9 ±16% of N_r (panel c). The majority of sumN was represented by HCN and NH_3, with acetonitrile (CH_3CN) higher than any of the other inorganics, HNCO, NO_2 or HONO. The NVOCs were also a larger fraction of N_r-NO than in the case of Fire 047 shown above, a feature that implies that more semi-volatile organic compounds, SVOC, survive these types of fires and could make a proportionally higher contribution to the N_r budget in this fire relative to Fire 047. FireLab results of particle organic carbon measurements (Jen et al., 2019) and field measurements in environments with a lot of dung burning (Jayarathne et al., 2018; Stockwell et al., 2016a) are consistent with a higher EF for particle organic carbon and by extension particle NVOC compounds. The quantity (N_r-NO)/N_r was relatively high and had less dynamic range than for fires with more flaming combustion like Fire 047.

An overall budget of N_r can be constructed for all of the stack fires through integrating the time profile of all the compounds and compound classes. The fire-integrated measurements of inorganic and NVOC species are listed in the Supplemental section as ratios to N_r for each stack fire (Table S1). The summary of all the fire integrated X_i/N_r fractions (where X_i is the N_r species or quantity) is given in Table 3 for all the fires for which we have a complete set of measurements (43 fires). In general, NO was the major species followed by NH_3, and the other inorganic N_r species, NO_2, HNCO, HONO, and HCN had individual contributions of 4.3 to 9.4 %. NVOC species were less than 5% of N_r on average. The unaccounted-for N_r, defined as (N_r-NO-sumN)/N_r had a median value of 14.3% and a mean (±std. dev.) of 15 (±10)%. Overall, 85% of N_r was accounted for by the gas phase measurements. The distribution of whole fire N_r residuals is plotted as a histogram in Figure 6. We expect the residual N_r was composed of either semi- or low-volatility compounds, or particle-bound N_r compounds, which we know are converted efficiently by the N_r catalyst

(Stockwell et al., 2018) but not detected by the instruments included in this analysis. Along these lines, there is some indication that the residual has a systematic variation with whole fire MCE, with higher residuals (up to 30%) observed at lower MCEs and higher (N_r – NO)/N_r (see Figure S1 a&b), which would be consistent with higher EF for SVOC at low MCE (Jen et al., 2019) and particle N_r having a higher contribution from NO_3^- (May et al., 2014), and perhaps particle ammonium or reduced-N_r compounds. In general, there is more particulate organic material emitted from fires at low MCE (Jen et al., 2019), so we would expect more particle N at low MCE to go along with that.

3.4 Systematic dependences of N_r composition on combustion processes.

The features noted in fires shown above, as well as the anti-correlation of MCE and (N_r-NO)/N_r lead to the question of whether there are systematic dependences in N_r-compound composition on fire stage that can be used to formally classify and/or potentially predict the relative emissions of N_r compounds. MCE has been used as a rough indicator of the relative amounts of flaming and smoldering combustion in a fire, with high MCE (~99%) being "pure" flaming, low MCE (~80%) being "pure smoldering," and an MCE of ~0.9 being roughly equal amounts of both (Sect. 2.1.1 in Akagi et al., 2011). It should be understood that "smoldering" in this framework is a lumped term that includes all non-flame processes such as pyrolysis, glowing, and distillation, which are the processes that produce gaseous fuel to support flaming (Yokelson et al., 1996). In addition, "pure flaming" is essentially the efficient oxidation of smoldering products before they enter the atmosphere. However, for MCE to predict flaming and smoldering N_r species well, the variable fuel N must be considered. For instance, NO_x is clearly produced by flaming based on its temporal profile, but fire-integrated EF_{NOx} may not correlate with MCE due to variable fuel N. In these cases, EF_{NOx}/fuel N or $\Delta NH_3/\Delta NOx$ may still correlate (or anti-correlate) well with MCE (e.g. Fig. 4 in Burling et al., 2010 or Yokelson et al., 1996). Finally, the flame chemistry involving NH_3, HNCO, and HCN both produces and destroys NO in a fashion that does not conserve N_r. This chemistry is explored in Figure 7 in which NOx, NH_3, HNCO, HCN, HONO, and CH_3CN ratios to N_r are plotted vs real-time MCE for Fire 047 as a typical example for fires that have a substantial range of MCEs (e.g. from 0.8 to above 0.98). The relationship between NH_3/N_r and MCE confirms that NH_3 is primarily a smoldering emission and NO_x/N_r increases with increasing MCE in a non-linear fashion that confirms it is primarily a flaming compound. Such a non-linear dependence has also been seen for other flaming-related quantities such as Elemental Carbon/TC or EF_{HCl} (Christian et al 2003; Stockwell et al., 2014). Most importantly, the variations of HNCO/N_r, HCN/N_r, HONO/N_r, and CH_3CN/N_r versus MCE do not arise dominantly from either regime as these are species that are likely produced by multiple pathways (e.g. "incomplete flaming", pyrolysis, possibly glowing). By "incomplete" flame chemistry we mean the production of incompletely oxidized products in flames such as the complex system of reactions shown in Fig. 1. These reactions involving HNCO, HCN and NH_3 both produce and destroy NO, while HONO is produced from reactions of NO and NO_2 that are faster at slightly lower temperatures, for example the three-body association reaction of NO with OH radical (Manion et al., 2015). Variable turbulence in the turbulent diffusion flames that are characteristic of open BB likely contributes to varying temperatures, and therefore, varying amounts of incomplete oxidation of the fuel N (Shaddix et al., 1994).

3.5 The PMF analysis of coniferous fuels

The complexity of the dependence of N_r speciation on combustion chemistry suggests that MCE is an insufficient model to use for applying lab results to real-world fire emissions (Stockwell et al., 2016a; Yokelson et al., 2013b). Accordingly, we employed the positive matrix factorization (PMF) method (see Methodology section) that has been used by a number of groups to probe the sources contributing to complex mixtures (see for example Ulbrich et al., 2009 Sekimoto et al., 2018). Our PMF results showed several general features, irrespective of the inclusion or exclusion of CO_2, CO and N_r. The emissions were best fit by three factors (with approximate descriptive names justified below and prime species): (1) a combustion (flaming) factor (abbreviated Comb-N), (2) a high temperature pyrolysis factor (HT-N), and (3) a low temperature pyrolysis factor, (LT-N). We use these terms in part to harmonize our discussion with the VOC results discussed by Sekimoto 2018. An example timeseries for the PMF analysis of a coniferous fuel with just the N_r species included is shown in Figure 8 for a realistic mix of lodgepole pine (Fire 063). In this case, several different Fpeak values were tried (-1, 0, +1) and runs with 100 different seeds (initial factor profiles) were performed. The results of those analyses (Figure S4) show that a 3-factor PMF result is robust. A PMF analysis was performed on the consolidated time series of all coniferous fuels fit using just the N_r species, as shown in Figure S5. In this case Fpeak=0 was used and the Q/Qexpected showed an inflection for the 3-factor solution at a value of 5.3 The three factors successfully describe the majority of the N_r-emissions where the difference between the measured and calculated mass is on average 5.1% for coniferous fuels and 4.6% for chaparrals as indicated in Table 4.

Several metrics of the PMF analysis quantify how the compounds or compound classes contribute to each factor. The 'loadings' of the three different factors, i.e. the contribution of compounds to each factor, for coniferous fuels are shown in Figure 9(a), and the distribution of a given compound or compound class amongst the three factors is shown in Figure 9(b) as normalized fraction. Normalized fraction is equal to the PMF-determined contribution of a compound to a factor, divided by the sum of the contribution of the compound to all three factors. The Comb-N factor contained NO, NO_2, and HONO, the HT-N factor had mostly HCN, HNCO, nitriles, with contributions from NO_2 and nitro compounds, and the LT-N factor contained NH_3, amines, amides and heterocyclics. Within the Comb-N factor there is some evidence that the relative amounts of HONO and NOx depend on fuel moisture. For example, the ratio HONO/NOx for whole fires shows some correlation with needle moisture in coniferous fires that were canopy fuels (Foliage and small woody biomass), as shown in Figure S6. This may be due to flame processes that interconvert NOx and HONO in the presence of water vapor of OH (see Figure 1).

Literature values from studies where flame temperature was measured are typically in the range of 1100 – 1200 °C (Taylor et al., 2004; Wotton et al., 2012), so we would assume that would constitute the upper range of our Comb-N factor. The radical chemistry involving HCN, HNCO and NH_3 starts to shut down below about 800-900°, according to the modeling of Glarborg et al., (2018), so we set 800°C as a lower limit for the Comb-N factor. The HT-N factor species are known to be produced by the intense pyrolysis of fuel N_r compounds (Hansson et al., 2004; Liu et al., 2018; Ren et al., 2010), which for these compounds becomes important at temperatures around 500-600°C. Accordingly, we estimate the temperature range for the HT-N factor at 500 – 800°C. The remaining LT-N factor results from mild pyrolysis and pertains to fire conditions of roughly 500°C and below, and was dominated by NH_3, amines, amides and some of the more complex organics (Koss et al., 2018). The names and temperature ranges are approximate and likely include processes that occur inside flames as part of the flame proper, as turbulent diffusive flames are highly variable in space and time.

3.6 The comparison of N-PMF factors to other fire parameters and VOC emission factors.

It is useful to explore the correlation of N-PMF factors with other fire indicators to determine relationships for parameterizing N_r emissions together with carbon and VOC emissions, in order to simplify how emissions might be parameterized in models. The Comb-N factor for coniferous fuels, which consisted of NO_x and HONO, would be expected to correlate with CO_2 but not as well with MCE since the latter includes an indicator of incomplete combustion. The timeseries of Comb-N along with CO_2 and with MCE for Fire 037 (ponderosa pine), are plotted in Figure 10. As expected they show an excellent correlation of Comb-N with CO_2 (R^2=0.942) since all the species are flaming compounds, but non-linear correlation of Comb-N with MCE (R^2=0.363) since the latter factors in a smoldering compound (CO), similar to the NOx/N_r vs. MCE plot for Fire 047 in Figure 7. The excellent correlation of Comb-N with CO_2 is a broadly applicable result, the R^2 parameters for all the fires shown in Figure S5 had an average of 0.898, and ranged from 0.806 to 0.966. As a consequence, we can conclude that CO_2 would be the best tracer for Comb-N in many western U.S. ecosystems where conifers predominate, provided ambient CO_2 backgrounds can be properly accounted for as described by Yokelson et al., (2013a).

Our Comb-N factor did not correspond to the high temperature VOC factor (HT-VOC) found by Sekimoto et al., (2018) in their pyrolysis study because our broader study includes flaming combustion, which produces NOx, and HONO, and almost none of the compounds classified as VOCs survive flaming conditions. However, the HT-N and HT-VOC factors are both linked to pyrolysis and were well correlated for many fires. An example of this is shown in Figure 11 for Fire 037, a sample that was broadly representative of ponderosa pine (i.e. canopy and litter). This result can be rationalized by the fact that while HT-VOC factors have large contributions from many more compounds that the N compounds measured here, they also have large contributions (>85%) from HCN, HNCO, and HONO, (in other words >85% of HCN, HNCO and HONO are found in the HT-VOC factor). Since the HT-N factors are also heavily weighted by HCN and HNCO, it is reassuring that both of these PMF analyses have independently identified these species as important contributors to the HT fire regime. The R^2 correlation coefficients between the HT-N and HT-VOC factors for the coniferous fires shown in Figure S5 averaged 0.866 and ranged from 0.419 to 0.959. As a consequence of this correlation, we can conclude that HCN is the best marker for the HT-N and HT-VOC factors in most western U.S. wildfires, since HCN is essentially inert on the timescales of fire plumes (Li et al., 2000). It should be noted that other nitriles, particularly acetonitrile, also show up in the HT-N factor, and acetonitrile has also been used as a tracer of biomass combustion. However, it has been shown that this acetonitrile signal can be obscured in urban or industrial areas by solvent usage, or can be quite small in woodstove emissions due to low N in the fuel (Coggon et al., 2016).

The correlations of LT-N and LT-VOC factors were not particularly high for most of the coniferous fires shown in Figure S5. The average R^2 was 0.427 with a range of between 0.072 and 0.827. The reasons for this lack of correlation are not clear, as NH_3, amines and amides appear predominantly in both LT factors, and the absolute concentrations of NH_3 are usually quite high in these fires relative to VOCs (Sekimoto et al., 2018). However, the LT-

VOC factor includes many more compounds with a variety of functional groups not found in the LT-N factor, so it appears that the VOC and N compounds have sufficiently different pyrolysis chemistry that the LT factors do not show much correlation. We conclude that NH_3 (and particle NH_4^+) will be the best marker for the LT-N factor in western U.S. coniferous wildfires, but the LT-VOC chemistry might not be captured reliably by this marker.

3.7 PMF analysis of chaparral fuels.

Chaparral is an important ecosystem of concern in wildfires that occur in central and southern California, and other areas of the southwestern U.S. The emissions from burning chaparral fuels (manzanita and chamise) collected at two sites in California were also analyzed as a group and yielded three separate factors in a fashion similar to the coniferous fuels (see Figure S7 for the PMF timeline). As with the coniferous fuels, there was essentially no change in the 3-factor solution with Fpeak, so Fpeak 0 was used, and the Q/Qexp was 3.8. The chaparral factors had slightly different composition (Figure S8), the combustion factor was mostly NO, with small amounts of HNCO, HONO and NH_3, the high temperature factor was dominated by NO_2 and included HONO, HCN, and HNCO, and the low temperature factor was mostly NH_3 with a slight amount of NO contributing. The NVOC species were found in both the medium and low temperature factors.

There was less similarity between the Comb-N factor and CO_2 emissions for chaparral fuels compared to those found for coniferous fuels, with an average correlation coefficient (R^2) of 0.689, with a range from 0.244 and 0.950. As a result, there may not be a simple conserved tracer for the combustion factor of these fuel types, however total odd nitrogen (NOy) which is NOx and all the compounds that are produced from NOx in the troposphere, may be useful as it is a reasonably conserved tracer in the absence of wet or dry deposition of particles. Correlation coefficients between the HT-N and HT-VOC factors were on average $R^2 = 0.551$, with a range 0.047-0.911. The correlations between LT-N and LT-VOC factors were in the same range for chaparral fuels as for coniferous, average $R^2 = 0.447$, range 0.028-0.827.

There were some fuels that do not sustain flaming combustion well, specifically duff, Yak dung and Indonesian peat. These fires exhibited little or no NO emission commensurate with minimal flaming combustion. Instead the emissions were mostly the pyrolysis products NH_3, (0.22 – 0.53 N_r fraction), and HCN (up to 0.32 N_r fraction for peat). It was also apparent that these fires also had unaccounted for N_r, close to, or just over 0.30 (Table S1). The distribution of N_r compounds in the one peat fire that we measured (Fire 055) is in line with those reported for fires measured in situ which showed relatively high EFs for HCN and NH_3 (Stockwell et al., 2016b; Stockwell et al., 2015).

3.8 Application to real-world fires.

The application of our N_r emissions results to real-world fires will depend somewhat on the nature of the information available on a particular fire, or fire complex. As a good starting point, or in the absence of detailed N and C analyses of fuels, a N_r/C ratio of 0.37% appears to capture most of the fires studied in this work. The N_r could be apportioned according to the results summarized in Table 3. Adjustments to those fractions can be made either by scaling slightly by average MCE, with the knowledge that intermediate species (HT-N pyrolysis species) such as HCN and HNCO do not scale in the simple manner that NH_3 and NO_x do. If measurements of marker compounds are available then CO_2, HCN, and the sum $NH_3 + NH_4^+$ can be used for the combustion, high-temperature pyrolysis, and low-temperature pyrolysis factors respectively.

4 Conclusions

Seventy-five stack fire experiments were conducted during the FIREX FireLab experiments in Fall, 2016. A range of fuels characteristic of the western U.S. was burned under conditions and in mixtures meant to represent authentic wildfire conditions, as closely as is possible in the laboratory. Total reactive nitrogen (N_r = all N-containing compounds except N_2 and N_2O) was measured along with a suite of N-containing compounds in order to obtain a budget for N_r-emissions and to examine relationships between fuels, combustion conditions, and emissions chemistry.

Natural convection wildfires do not burn hot enough to produce NO_x from N_2 and O_2, so all N_r emissions come from the fuel N. Almost all of the fires representative of North American ecosystems had emissions that clustered around a N_r/C ratio of 0.37%, which can serve as a starting point for scaling emissions from these ecosystems. Comparing total N_r and total carbon emissions with the N/C ratios of both the original fuel and remaining ash allowed us to estimate that an average of 68% (±14%) of the fuel nitrogen ends up as N_2 and N_2O. This loss of nitrogen can be used to estimate how much fuel nitrogen ends up as N_r. Of the remaining N emitted as N_r, approximately 85% (±10%) was accounted for by individually measured gas-phase species, while the rest was most likely particle-bound NH_4^+ and NO_3^-, with a smaller contribution from low-volatility species or other species such as cyanogen (Lobert and Warnatz, 1993), that were not quantified by the instruments for individual measurements we used in this study. The speciation and modeling of Nr we present promotes accurate modeling of fire plume chemistry since the photochemistry of many fire plumes is NOx-limited, and NH_3 is an important contributor to particle chemistry.

The individual N_r species composition normalized to Total N_r, to account for fuel N variability, correlated monotonically with flaming versus vs. smoldering combustion as indicated by modified combustion efficiency (MCE) for some species (e.g. NH_3, NO_x). Other species, such as HCN and HNCO, peaked at intermediate MCE values. Positive matrix factorization (PMF) showed that all the measured N_r emissions from the main two categories of fuels, conifers and chaparral, grouped into three mixtures (factors), roughly attributed to temperature: combustion (NOx, HONO), high temperature (HNCO, HCN, nitriles), and low temperature (NH_3, amines, amides). Chemical kinetic and pyrolysis considerations set the temperature ranges for these regimes at approximately 800-1200°C, 500-800°C and <500°C respectively.

This paper connects mechanistic aspects of N combustion chemistry to the budget of N_r emissions from biomass burning. The emission composition measurements detailed here give useful information concerning what the initial conditions will be in actual fire plumes. These results suggest that for coniferous fuels characteristic of the western U.S. CO_2 is the best marker for flaming combustion, HCN is the best marker for high temperature pyrolysis processes, and NH_3/NH_4^+ is the best marker for low temperature pyrolysis processes. The HT-N and HT-VOC pyrolysis factors showed high degree of correlation especially for coniferous fuels, which can simplify how these different classes of emissions can be estimated. Results from less comprehensive field experiments can be combined with this emissions information to improve the representation of N_r-chemistry in the modeling frameworks needed to predict fire plume chemistry and impacts.

Data availability

The FIREX Firelab 2016 data are available at: https://esrl.noaa.gov/csd/groups/csd7/measurements/2016firex/FireLab/DataDownload/. The descriptions of the measurements can be found here: https://esrl.noaa.gov/csd/groups/csd7/measurements/2016firex/FireLab/dataidtable.html. The complete ash analyses are available on request.

Author Contributions

JMR, RY, CW and JdG designed the research. The measurements were conducted by JMR, CS, CW, RJY, JdG, YL, VS, ARK, KS, MMC, BY, KJZ, SSB, CS, and SHD. All authors contributed to the discussion and interpretation of the results and writing the paper.

Competing interests

Joost de Gouw worked as a consultant for Aerodyne Research during part of the preparation phase of this paper.

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Any mention of brand names or manufacturers is for information purposes only and does not constitute an endorsement.

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Table 1. Nitrogen compounds observed in the FIREX FireLab 2016 Study.

Compound/Class	Importance	Measurement Method	Method Reference
Total Reactive N	Total available for atmospheric reactions	Catalytic Conversion NO/O$_3$ chemiluminescence	Stockwell et al., 2018
Nitric Oxide	Major "flaming stage" product, oxidant production	NO/O$_3$ chemiluminescence OP-FTIR (Open Path Fourier Transform Infrared)	Williams et al., 1998 Selimovic et al., 2018
Nitrogen Dioxide	Atmospheric oxidant production	OP-FTIR, ACES (Airborne Cavity-Enhanced Spectometer)	Stockwell et al., 2014, Min et al., 2016, Zarzana, et al., 2018
Nitrous Acid	HO$_x$ radical source	OP-FTIR, ACES	Stockwell et al., 2014, Min et al., 2016, Zarzana et al., 2018
Nitric Acid[1]	Particle precursor	OP-FTIR	Yokelson et al 2009, McMeeking et al 2009
Hydrogen Cyanide	Flame chemistry, Atmospheric tracer, Toxicity	OP-FTIR, PTR-ToF-MS (Proton Transfer Reaction Time of Flight Mass Spectrometer)	Selimovic, et al., 2018 Koss, et al., 2018
Isocyanic Acid	Flame chemistry, Toxicity, Health effects	PTR-ToF-MS	Koss, et al., 2018
Ammonia	Major "smoldering stage" product, Main atmospheric base, Particle formation	OP-FTIR	Selimovic, et al., 2018
NVOCs: Amides[2] Amines[3] Heterocyclics[4] Nitriles[5] Nitro compds[6]	Brown carbon, Toxicity, Tracers	PTR-ToF-MS, GC/MS (Gas Chromatography Mass Spectrometry), I$^-$ CIMS (Iodide ion Chemical Ionization Mass Spectometer.	Koss, et al., 2018 Gilman et al., 2015 Lerner et al., 2017 Lee et al., 2014

1). The OP-FTIR has a 10ppbv detection for gas phase HNO$_3$, but HNO$_3$ was not observed above detection limit.
2). Ethylamine, methanimine, propeneamine, sulfinylmethanamine, trimethylamine, buteneamines
3). Formamide, acetamide, methylmaleimide
4). C$_2$-pyrroles, dihydropyridine, ethynylpyrrole, methylpyridine, methylpyrrole, pyridinealdehyde, 4-pyrindinol, vinylpyridine
5). Acetonitrile, acrylonitrile, benzonitrile, butanenitrile, butynenitrile, benzoacetonitrile, C$_7$acrylonitrile, C$_8$-nitriles, heptylnitrile, furancarbonitrile, methylbenzoacetonitrile, pentylnitriles, propanenitrile, propynenitrile, butenenitrile, methylisocyanate.
6). Butenenitrates, nitrobenzene, nitroethane, nitroethene, nitrofuran, nitromethane, nitropropanes, nitrotoluene.

Table 2. Compounds and compound classes used in the PMF analyses and their corresponding errors.

Compound or Class	unit	Estimated error
NH_3	ppbv	5% + 2 ppbv
NO	ppbv	10% + 1 ppbv
NO_2	ppbv	10% + 0.2 ppbv
HONO	ppbv	20% + 1 ppbv
HCN	ppbv	15% + 0.2 ppbv
HNCO	ppbv	15% + 0.2 ppbv
Nitriles	ppbv	20% + 0.2 ppbv
Amines	ppbv	20% + 0.2 ppbv
Amides	ppbv	20% + 0.2 ppbv
Nitro-compounds	ppbv	20% + 0.2 ppbv
Heterocyclics	ppbv	20% + 0.2 ppbv

Table 3. Summary of X_i/N_r Measurements for all Stack Burns[1]

Quantity	**Average ±(std dev) %**
NO/N_r	34.5 (16.6)
NO_2/N_r	9.4 (6.2)
$HNCO/N_r$	6.0 (2.9)
$HONO/N_r$	4.5 (2.2)
HCN/N_r	4.3 (2.3)
NH_3/N_r	19.3 (6.7)
$NVOC/N_r$	4.3 (2.8)
$(N_r\text{-sumN})/N_r$	15.2 (9.8)

1). Not every measurement was available for every fire, consequently the values do not add up to exactly 100%.

Table 4. Residuals of the PMF analyses by fuel, as percent of total signal

Fuel	Total Number	Component	Fire Number	Residual (%), avg (stdev)
Ponderosa Pine	9	Realistic (mix)	Fire 37,59,72	3.8 (± 1.4)
		Canopy (pure)	Fire 19[a],39	
		Litter (pure)	Fire 38	
Lodgepole Pine	5	Realistic	Fire 07[a],58,63	5.1 (±3.1)
		Canopy	Fire 40	
		Litter	Fire 41	
Douglas Fir	4	Realistic	Fire 14[a],57	6.8 (±3.1)
		Canopy	Fire 18	
		Litter	Fire 43[a]	
SubAlpine Fir	5	Realistic	Fire 47,67	6.6 (±2.3)
		Canopy	Fire 15,23	
		Litter	Fire 51[a]	
Engelmann Spruce	2	Realistic	Fire 08[a]	3.1 (±1.9)
		Canopy	Fire 25	
Chamise (San Dimas, CA)	2	Canopy	Fire 24,29	4.4 (±2.7)
Chamise (North Mountain, CA.)	2	Canopy	Fire 27,32	4.2 (±1.0)
Manzanita San Dimas, CA)	2	Canopy	Fire 30,33	4.8 (±2.1)
Manzanita (North Mountain, CA.))	2	Canopy	Fire 28	5.1

a-Excluded from Batch 2

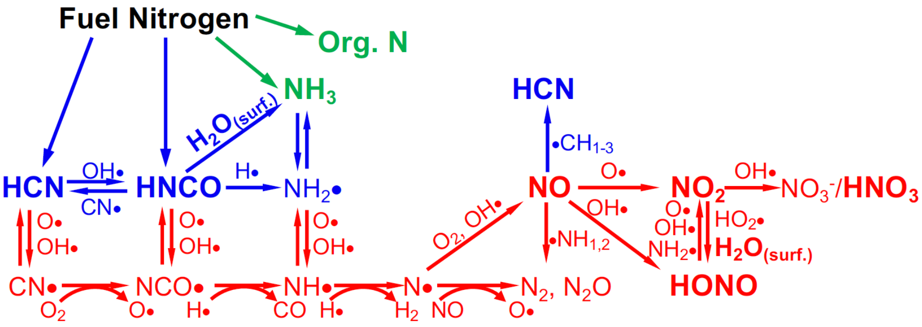

Figure 1. Schematic of the combustion chemistry of the small molecules that are emitted from BB and represent sources and sinks of reactive nitrogen (N_r), adapted from (Glarborg et al., 2018; Lobert and Warnatz, 1993; Lucassen et al., 2012; Manion et al., 2015). $H_2O_{(surf)}$ denotes the combination of H_2O and a surface to facilitate the reaction. Red color indicates the highest temperature (combustion) processes, blue indicates intermediate temperature processes and green indicates the lowest temperature processes. The species that are measured in this work are shown in bold and slightly larger text.

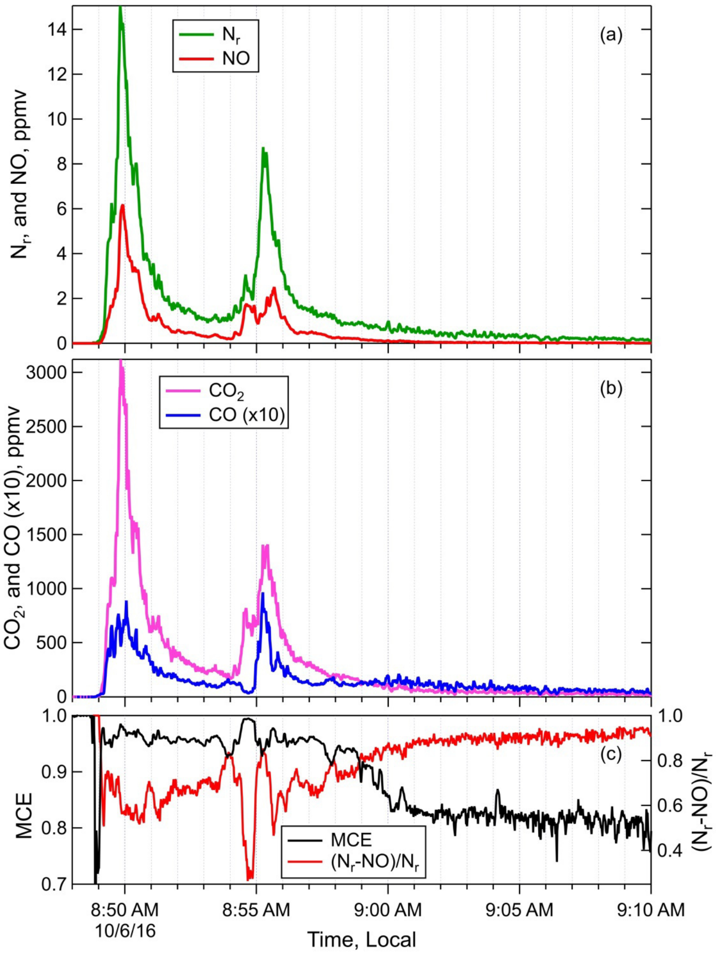

Figure 2. Timelines of the N_r, NO (panel a), ΔCO_2, ΔCO (panel b), MCE and $(N_r\text{-NO})/N_r$ (panel c) measured during Fire 004, a ponderosa pine realistic mix sample. Note that ΔCO is plotted at x10 the measured abundance for clarity.

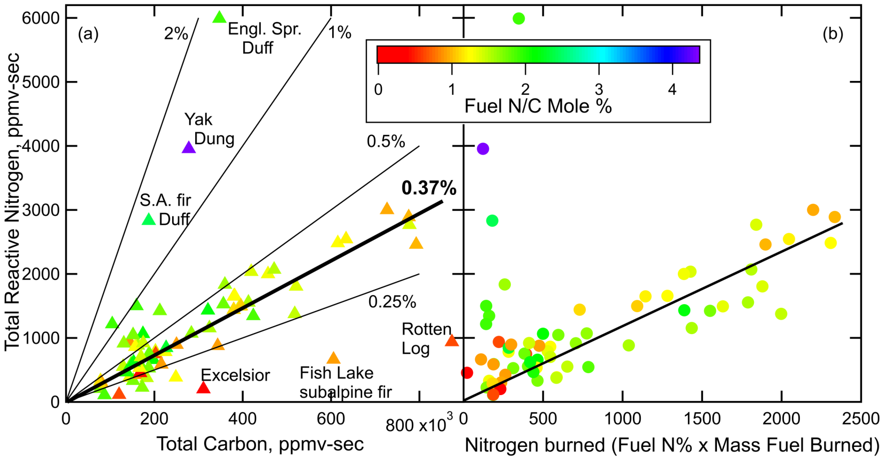

Figure 3. Integrated N_r versus integrated Total Carbon (panel a), and versus nitrogen burned based on fuel nitrogen content and mass of fuel burned (panel b). The points are colored by fuel nitrogen to carbon ratio. Note that the x and y scales on panel (a) are different by more than a factor of 100.

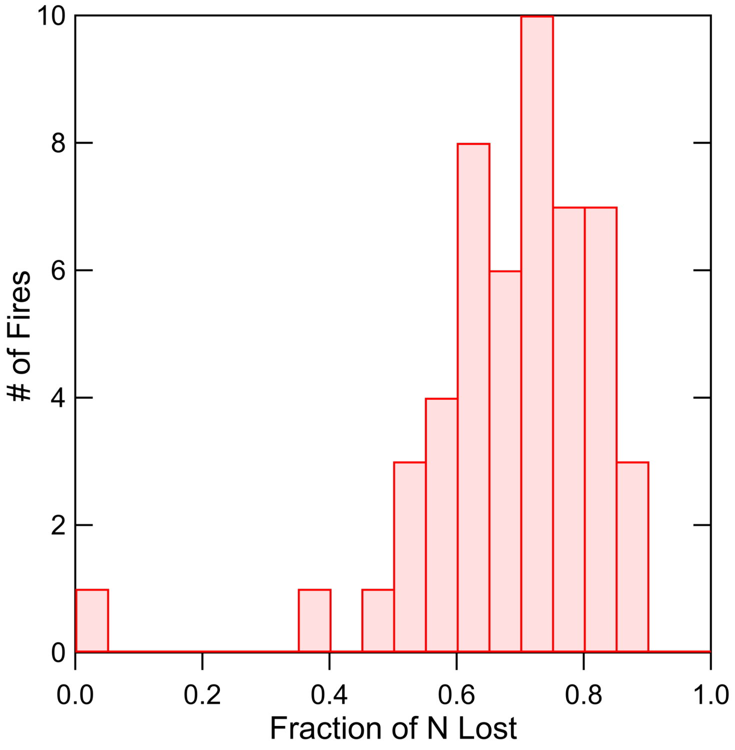

Figure 4. The histogram of the fraction of N loss to N_2 and N_2O estimated from the mass balance analysis described in the Supplemental Materials (52 burns).

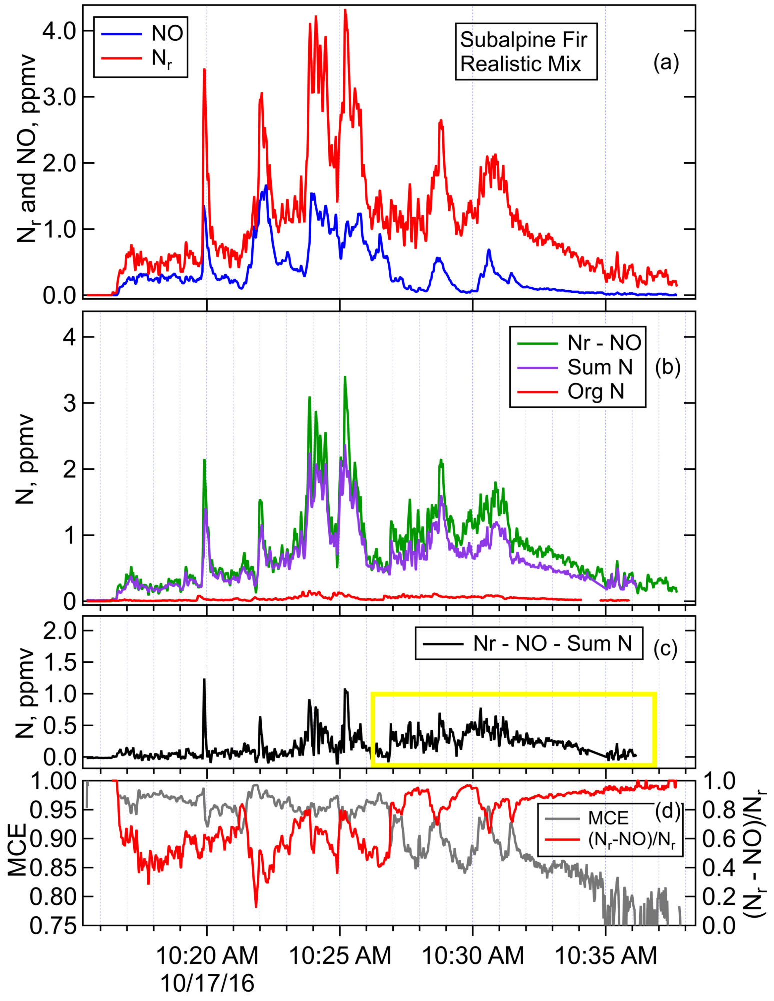

Figure 5. Timelines of N_r and NO (panel a), N_r – NO, the sum of all measures N species except for NO (panel b), residual of N_r minus all measured N species (N_r – NO – Sum N, panel c), and MCE and (N_r – NO)/N_r (panel d) for Fire047, subalpine fir realistic mix. The yellow box highlights the area of higher residual N_r that corresponds to more smoldering emissions.

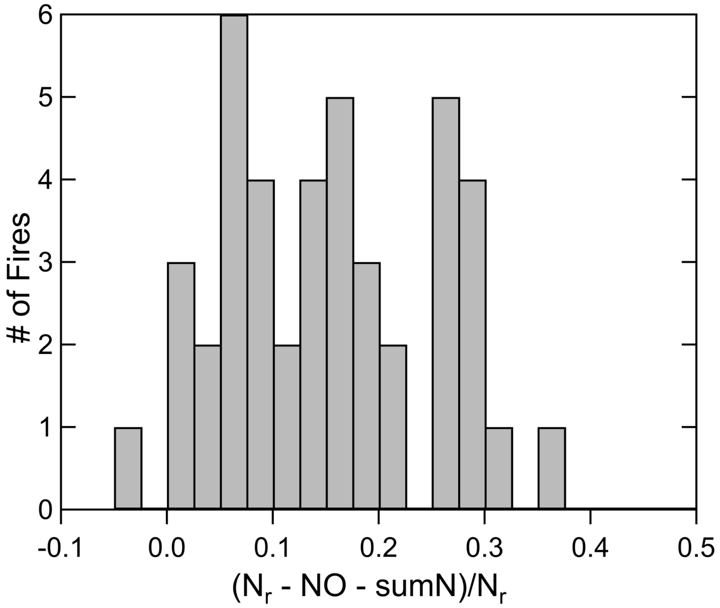

Figure 6. A histogram of the residual N for all the stack fires during the 2016 FireLab study for which there are FTIR, ACES and PTR-ToF measurements (n=43). The median is 0.143, and the mean (±std dev) was 0.15 (±0.10).

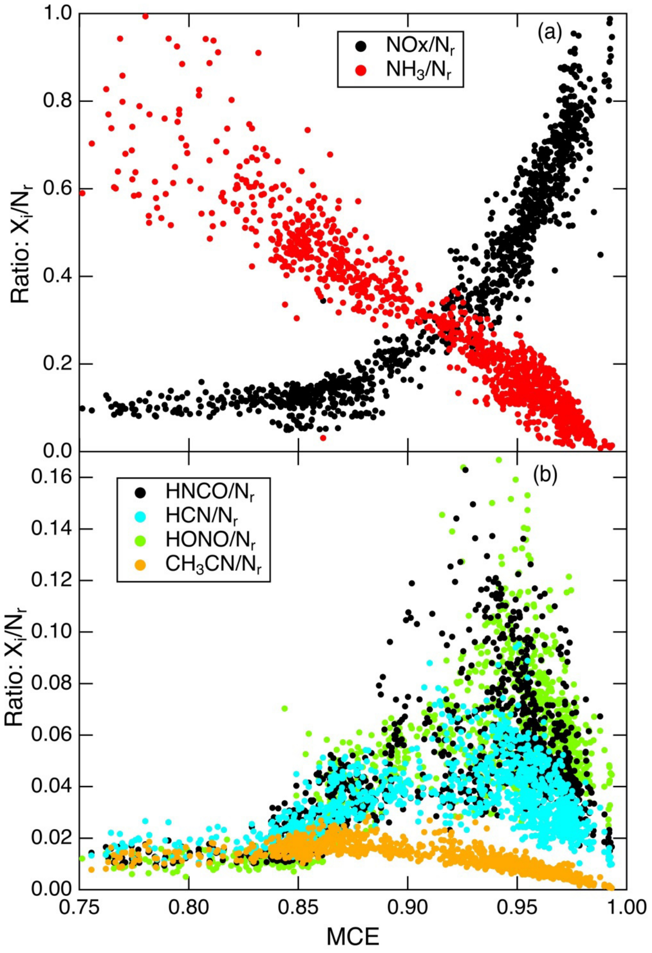

Figure 7. The relationships between NO$_x$/N$_r$ and NH$_3$/N$_r$ vs MCE (panel a), and the HNCO/N$_r$, HCN/N$_r$, HONO/N$_r$, and CH$_3$CN/N$_r$ vs MCE (panel b) for Fire 047.

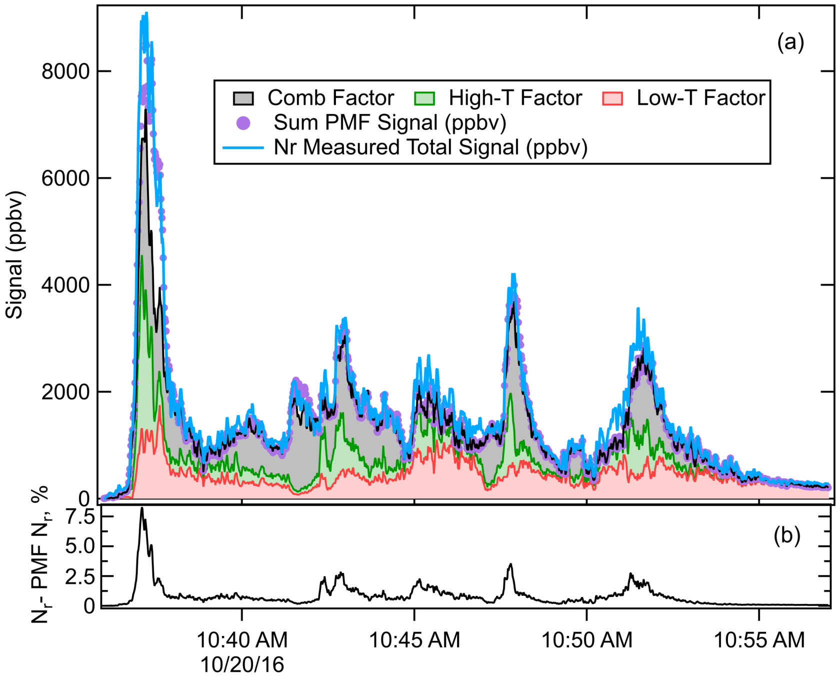

Figure 8. Pane (a), the measured N_r signal for Fire 063 (lodgepole pine) (blue line), the sum of the signal reconstructed by the PMF (purple points) and the three PMF factors: combustion (grey), high temperature (green) and low temperature (red), plotted in a stacked fashion (i.e. added on top of one another). Panel (b) the "residual" of the PMF fit consisting of the measured N_r signal minus the N_r signal reconstructed by the PMF, as a percentage of the N_r signal.

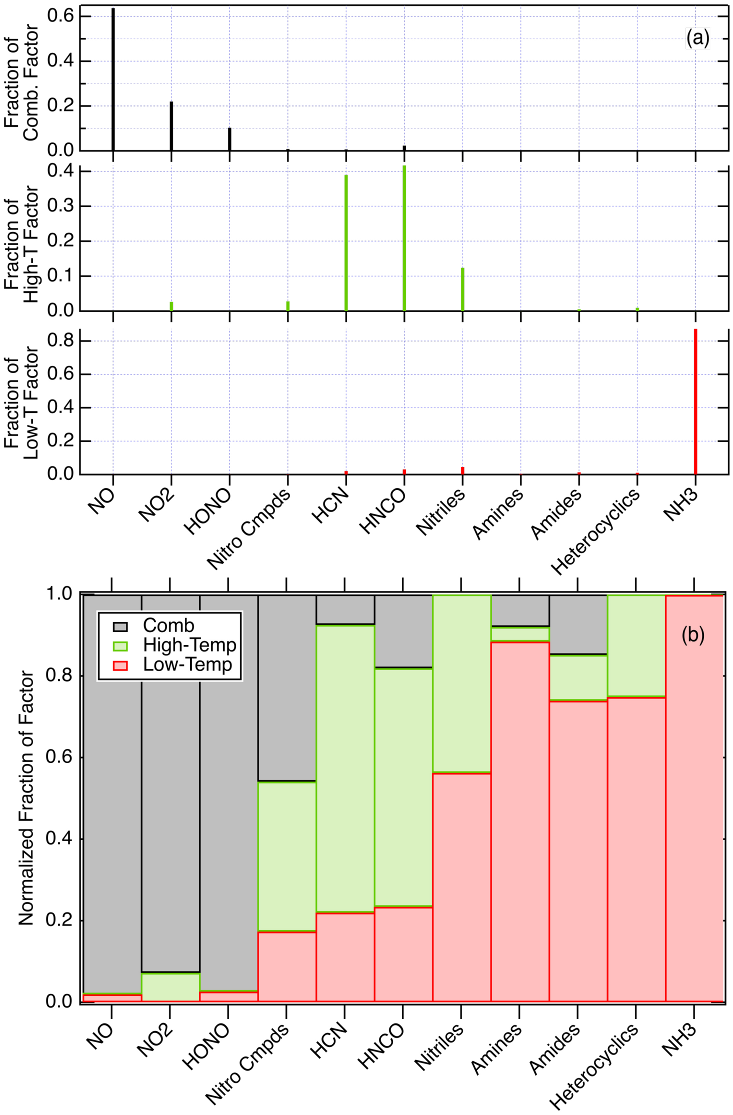

Figure 9. The contributions of nitrogen species to the factors that simulate the emissions from coniferous fuels shown in Figure S2 (panel a), and the fraction of each compound or class found in each factor (panel b).

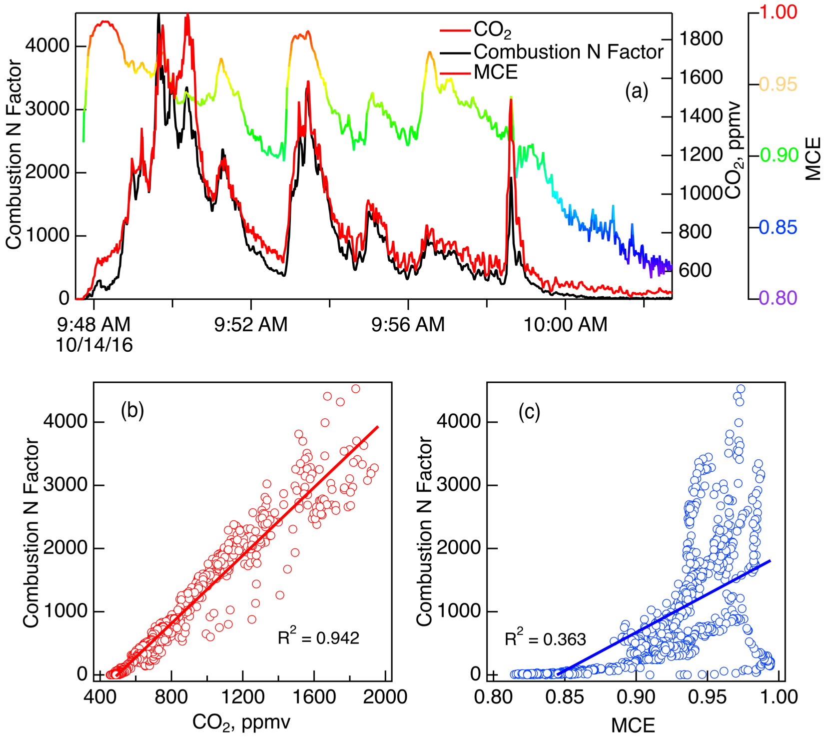

Figure 10. Comparisons of the N-PMF combustion factor (Comb-N) with CO$_2$ and MCE (Panel a) for Fire 037 (ponderosa pine). Panel (b) shows the scatter plot of the Comb-N factor versus CO$_2$ and panel (c) shows the scatter plot of Comb-N factor versus MCE.

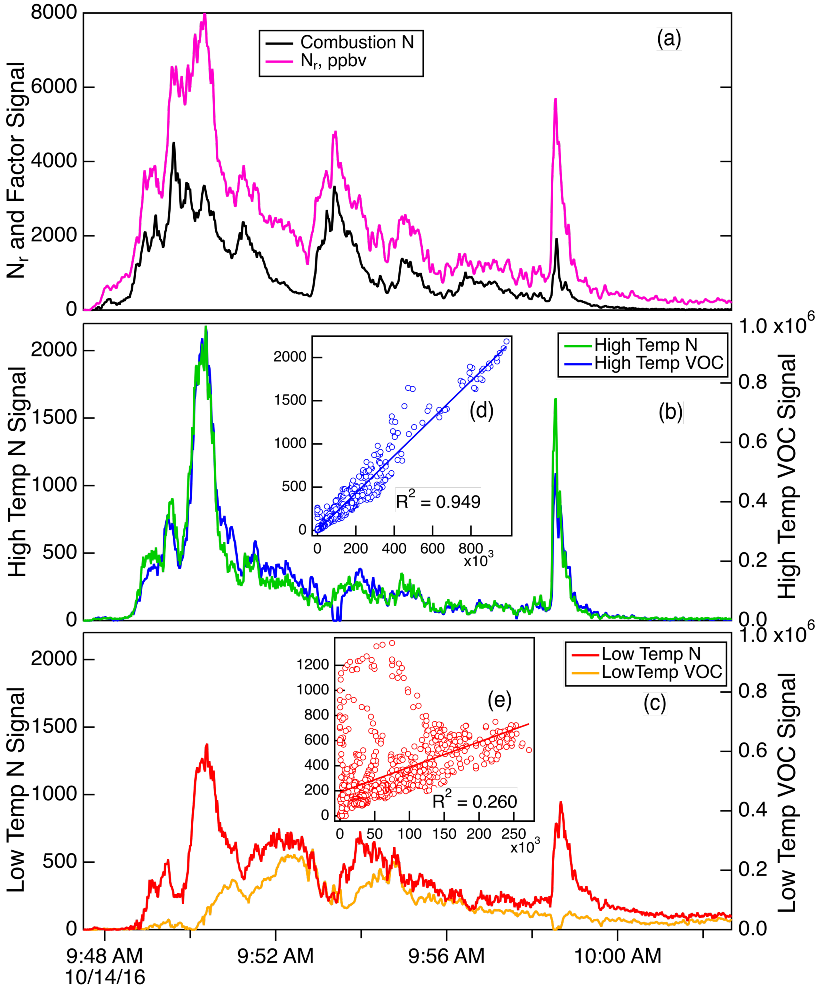

Figure 11. Details of the PMF factors for Fire 037 (ponderosa pine). Panel (a) shows the total N_r signal (magenta) and the Comb-N factor (black), panel (b) shows the HT-N factor (green) and HT- VOC factor (blue), and panel (c) shows the LT-N factor (red) and LT-VOC factor (orange). The insets (panel d) show the correlation of the two HT factors and the correlation between the two LT factors.

Supplemental Material

1. Determination of the diffusion and dispersion time constants of the NO and N_r measurements

The effect that diffusion and dispersion had on the effective time constants of the NO and N_r measurements was estimated from well understood transport and diffusion equations, and was determined experimentally from comparison of these measurements to the NO and NH_3 measurements made by the OP-FTIR at the sampling point at the top of the stack. The effects that sampling the atmosphere into a long tube has on the integrity of temporal information has been discussed by Karion et al., (2010). The figure of merit here is the root-mean square of the distance a gas molecule travels during the time the air sample transits from the stack to the instrument. This distance, X_{rms} can be calculated;

$$X_{rms} = (2Dt)^{1/2} \qquad \text{Eq S1.}$$

where D is the bimolecular diffusion coefficient of the analyte in air, and t is the time the diffusion is allowed to happen, in this case the 14 sec transit time from the stack to the instrument. Longitudinal mixing due to laminar flow, sometimes called dispersion, can add to the effective diffusion and can be estimated using the following relationship:

$$D_{eff} = D + a^2V^2/48D \qquad \text{Eq S2.}$$

where a is the inner radius of the tube, and V is the average flow velocity. Substituting the values of a and V, and using D_{NO} = 0.23 cm^2/sec (Tang et al., 2014), results in $X_{rms} \cong$ 40cm. The linear velocity of the gas within the tube is 120 cm/sec, so based on simple diffusion and laminar flow dispersion, the effective time constant of the data acquired at 1 Hz would be degraded to about 2 second or so.

The comparison of the 1 Hz NO and N_r data with NO and NH_3 measurements acquired at the top of the stack by the OP-FTIR provides a useful means to check the effective time constant.

Figure S1 shows the comparison of the chemiluminescence instrument measurements with the NO and NH_3 OP-FTIR measurements. The OP-FTIR had an effective sample acquisition/averaging time of 1.26 sec, so a 3-point smoothing of OP-FTIR signals results in an effective time constant of approximately 4 seconds.

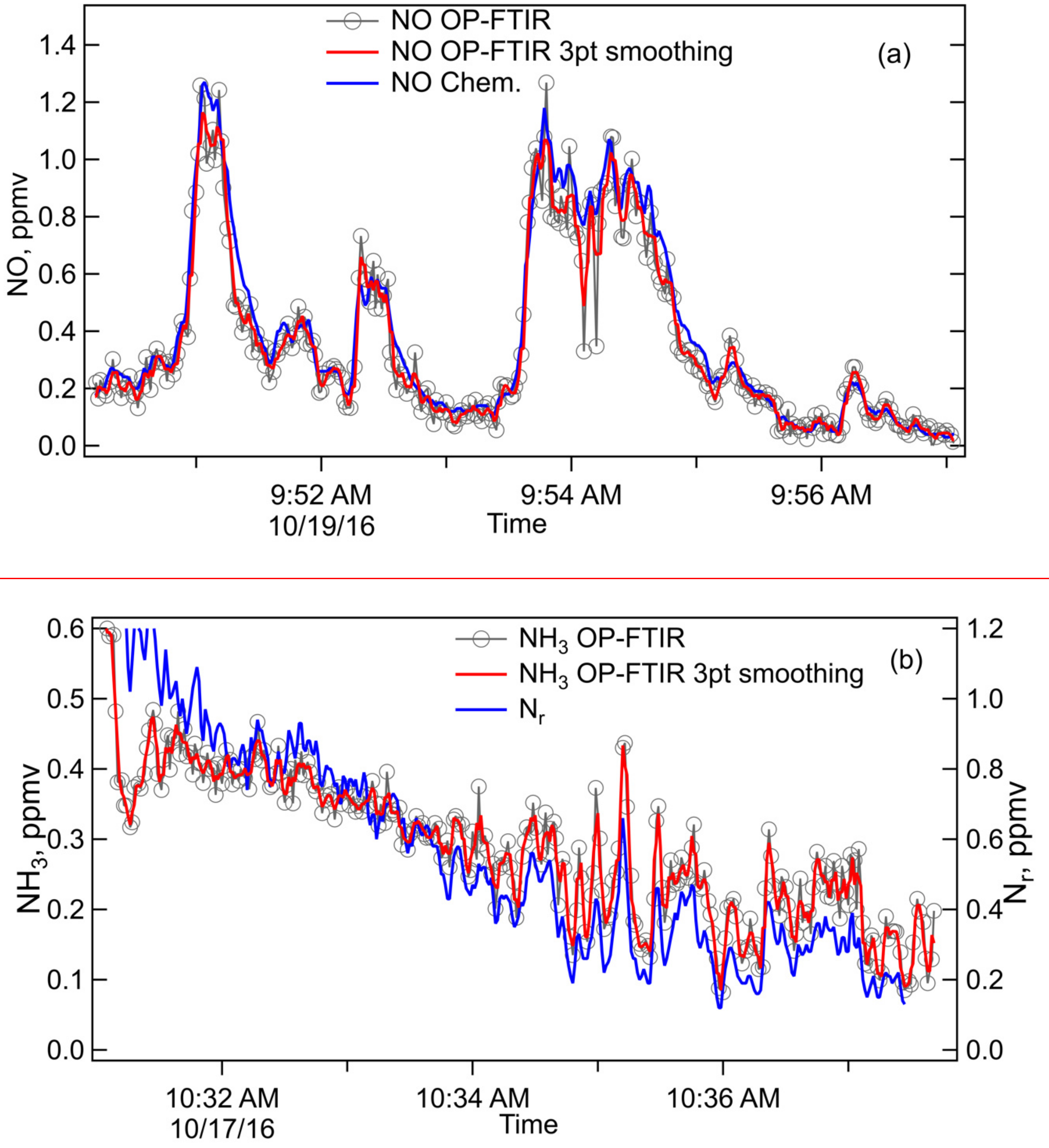

Figure S1. Comparison of the NO chemiluminescence measurement with that of the OP-FTIR (Panel a) for Fire 057, and comparison of the N_r measurement at the end of Fire 047 with the NH_3 measurement from the OP-FTIR (Panel b). Both the OP-FTIR 1.26 sec and the OP-FTIR data smoothed with a 3-pt box car method are shown.

2. Estimating the N lost to N_2 and N_2O.

The loss of N to N_2 and N_2O in the stack fires was estimated using the fuels data compiled in the Supplemental Material of Selimovic et al., [2018], and the ash data listed in

Table S1 of this Supplemental. The fuels data used in the analysis include: Total Fuel Mass, Total Residual Mass, %N Fuel (by weight), %C Fuel (by weight), and the ash data used in the analysis include: the ratio Ash/Burned Fuel, %N Ash (by weight), %Total C Ash (by weight). The gas phase measurements used for the analysis include: Total Reactive Nitrogen (N_r) reported here, and Total Carbon ($CO_2 + CO + CH_4 + \Sigma NMOC$ + Particle Carbon), calculated in the manner described by Selimovic et al., [2018]. In the calculations below, we assume the Ash/Burned Fuel, %N Ash and %C Ash are the same for the stack burns as the quantities measured during the room burns. These assumptions add only a modest level of uncertainty since the fuels burned in each set of experiments were subsets of large samples of each fuel type, and the use of Ash/burned fuel removes some of the variability in fire conditions and extent, as it accounts for unburned residual fuel. Another source of uncertainty is the application of fuel moisture measurements. In general, the correction for fuel moisture applies equally to foliage (needles) and woody biomass, but there are occasions where those were not equal or the residual fuel was more heavily represented by woody biomass. Residual masses were often 10% of the initial fuel mass, but sometimes as high as 50% of initial mass. Considering these factors, we estimate an uncertainty in the mass balance calculations to be ±25%.

The mass balance equations for Nitrogen and Carbon are;

Mass N emitted = Mass Total Fuel *%N Fuel – Mass Ash*%N Ash – Mass Unburnt residual *%N Fuel = Mass ($N_r + N_2 + N_2O$) Eq. S3

Where: Mass Unburnt residual = Mass Total Residual – Mass Ash Eq. S4.

and

Mass C emitted = Mass Total Fuel *%C Fuel – Mass Ash*%C Ash – Mass Unburnt residual *%C Fuel = Mass ($CO_2 + CO + CH_4$ +NMOC + Particle C) = Mass Total C Eq. S5

Where: Mass Unburnt residual = Mass Total Residual – Mass Ash Eq. S6.

There are measured concentrations of N_r, and Total C, however there were not accurate measurements of the actual flow rates of air up the stack. The concentrations (mixing ratios) of N and C species are related to mass flow by several constants, e.g. pressure, temperature, Avogadro's number, all of which are the same for both N and C, except for the atom weights. As a consequence, we can use the ratios of concentrations to obtain the following relationships;

$$\frac{(N_r+N_2+N_2O)}{\text{Total C}} = \frac{(\text{Mass Total Fuel} *\%\text{N Fuel} - \text{Mass Ash}*\%\text{N Ash} - \text{Mass Unburnt residual} *\%\text{N Fuel})/14\text{g}}{(\text{Mass Total Fuel} *\%\text{C Fuel} - \text{Mass Ash}*\%\text{C Ash} - \text{Mass Unburnt residual} *\%\text{C Fuel})/12\text{g}} \quad \text{Eq.S7}$$

Recognizing that;

$$\frac{(N_2+N_2O)}{\text{Total C}} = \frac{(\text{Mass Total Fuel} *\%\text{N Fuel} - \text{Mass Ash}*\%\text{N Ash} - \text{Mass Unburnt residual} *\%\text{N Fuel})/14\text{g}}{(\text{Mass Total Fuel} *\%\text{C Fuel} - \text{Mass Ash}*\%\text{C Ash} - \text{Mass Unburnt residual} *\%\text{C Fuel})/12\text{g}} - \frac{N_r}{\text{Total C}} \quad \text{Eq.S8}$$

The ratio of Eqs. S8 and S7 gives;

$(N_2+N_2O)/(N_r+N_2+N_2O)$ = The fraction of N lost as N_2 and N_2O, estimated from fuel and ash composition and the measured quantity N_r/Total Carbon.

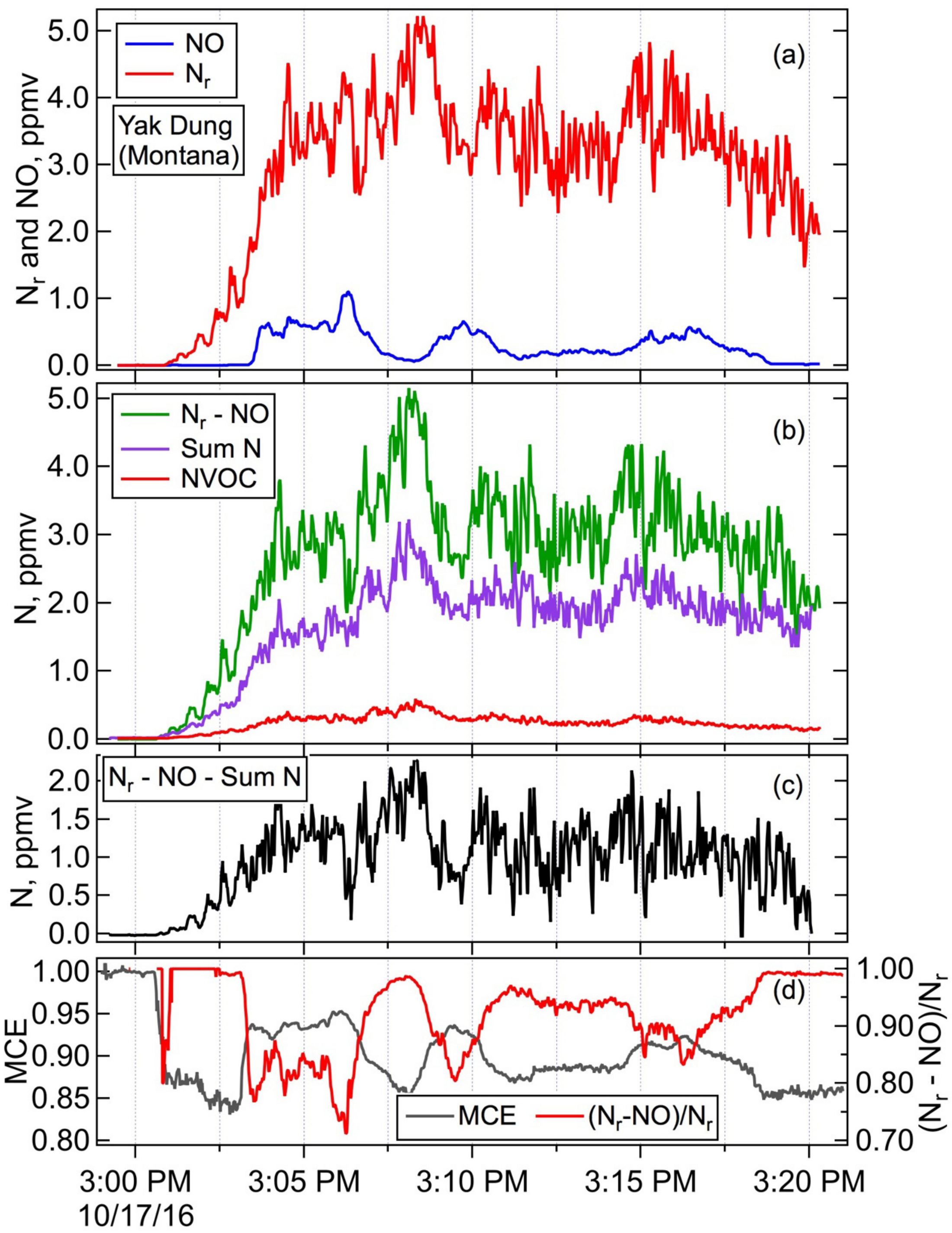

Figure S2. Timelines of N$_r$ and NO (panel a), N$_r$-NO, the sum of all measured N$_r$ species except for NO (panel b), and residual of N$_r$ minus all measured N species (N$_r$-NO-Sum N, panel c) and MCE and (N$_r$-NO)/N$_r$ (panel d) for Fire050, Montana yak dung.

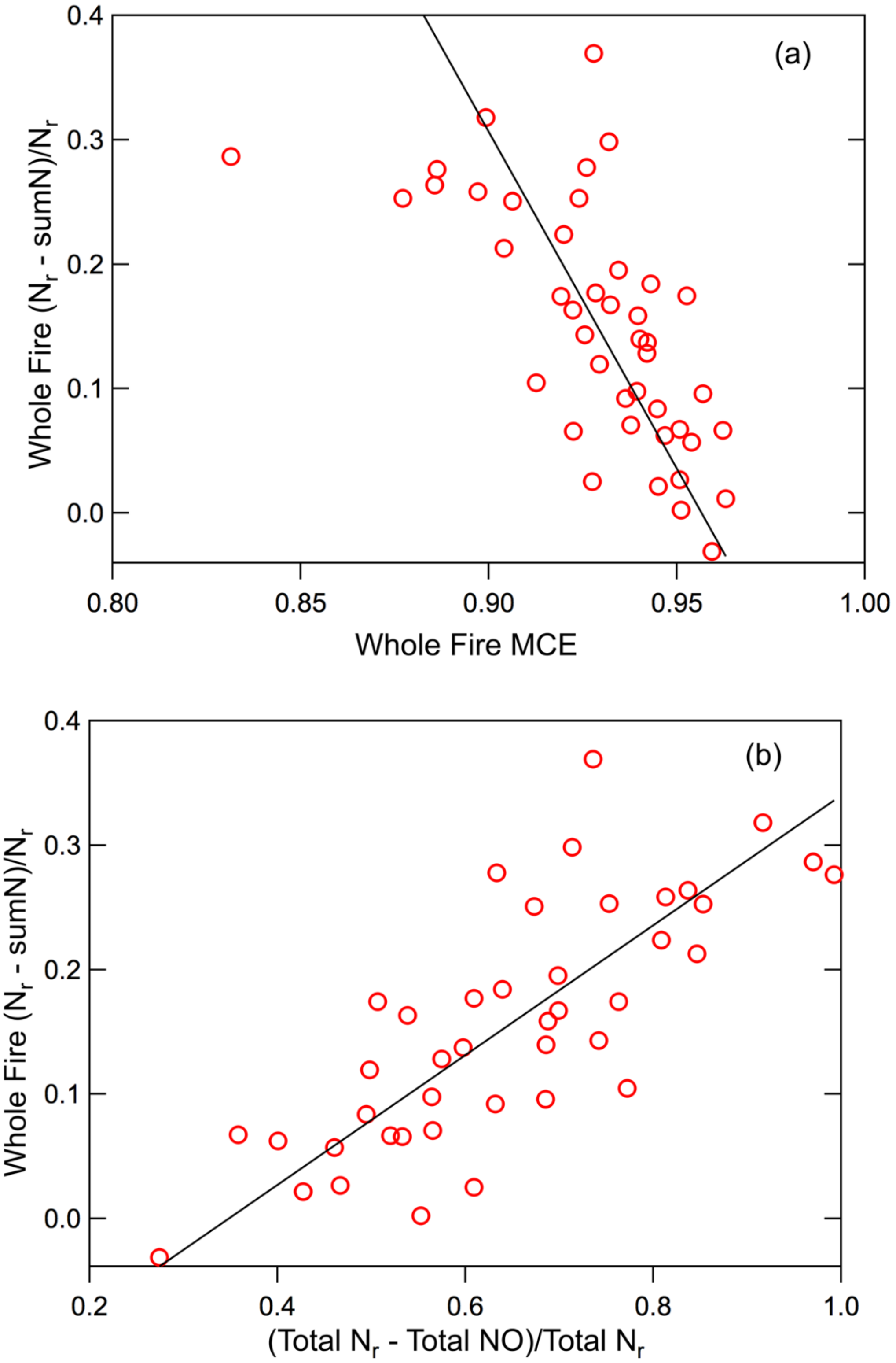

Figure S3. The relative amounts of residual N_r vs MCE (a) and vs $(N_r\text{-sumN})/N_r$ (b) for whole fires. The lines are orthogonal-distance-regression fits that assume uncertainty in each variable.

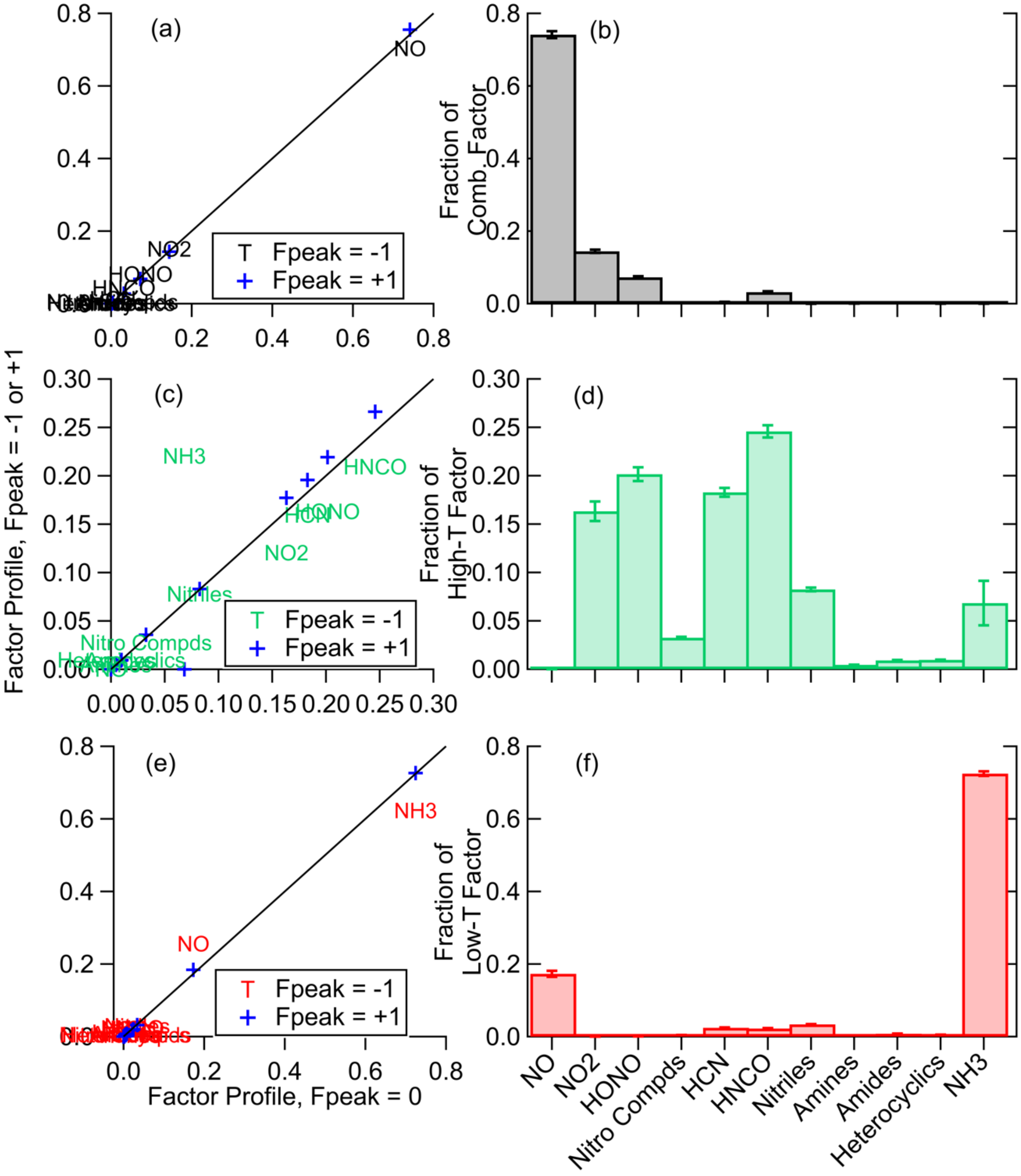

Figure S4. Details of the PMF analysis of Fire 063. Figures S4 a, c and e show that the Fpeak=0 solution is stable compared to Fpeak -1 and +1. Figures b, d, and f show that the three factor solution is robust with respect to different initial factor profiles (seeds) for 100 different runs.

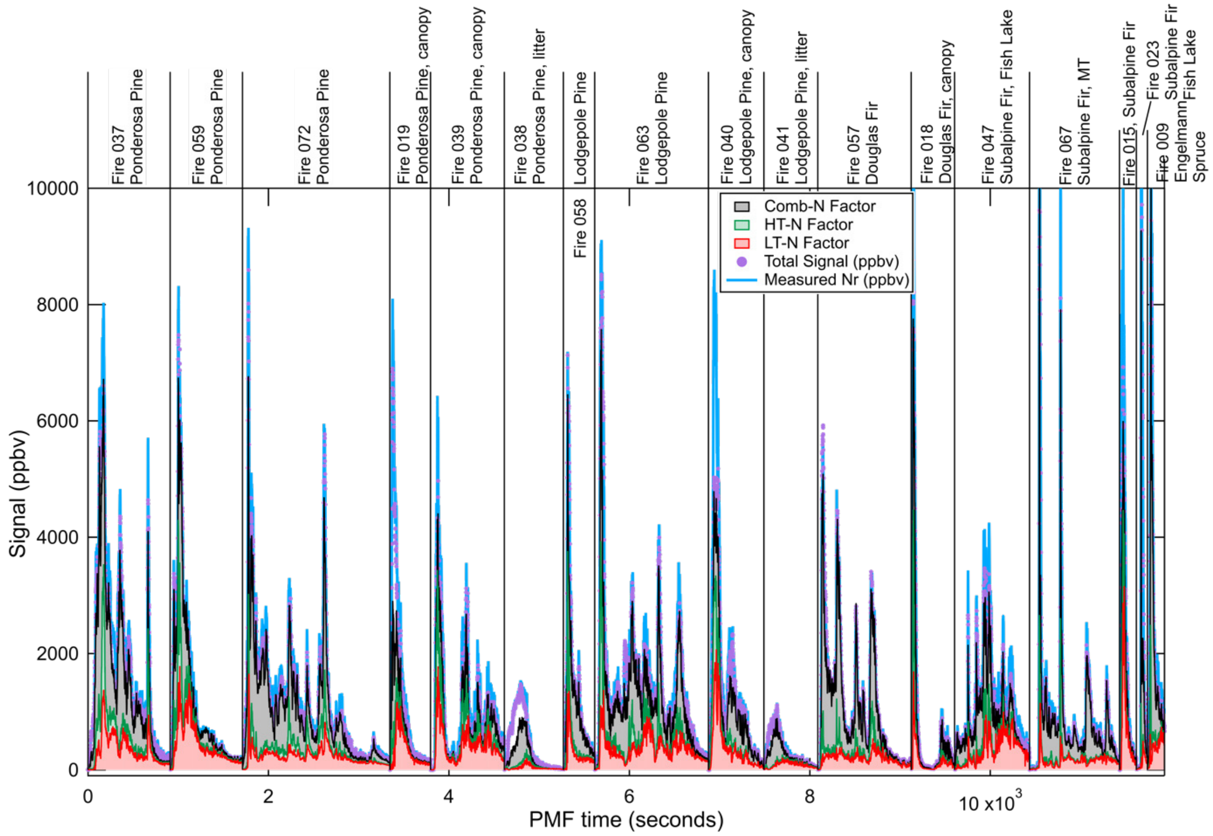

Figure S5. Combined PMF timeline for the fires that involved coniferous fuels. The measured N_r is shown as a blue line, the total of N_r compounds used in the PMF is shown as purple points, and Comb-N (grey), HT-N (green), and LT-N (red) factors plotted stacked on top of one another. The vertical lines show where individual fires start and stop.

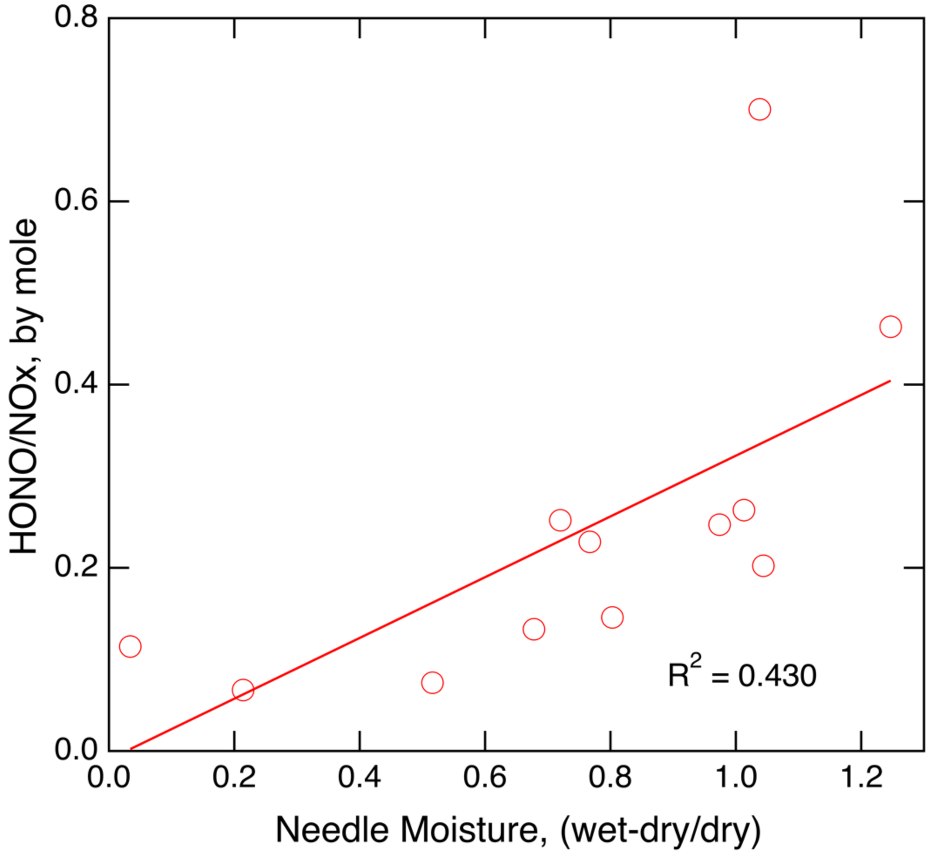

Figure S6. The correlation of HONO/NOx (by mole) with needle moisture for fires that were canopy fuels only (Fires 015, 017, 018, 019, 020, 023, 025, 039, 040, 044, 045, and 064).

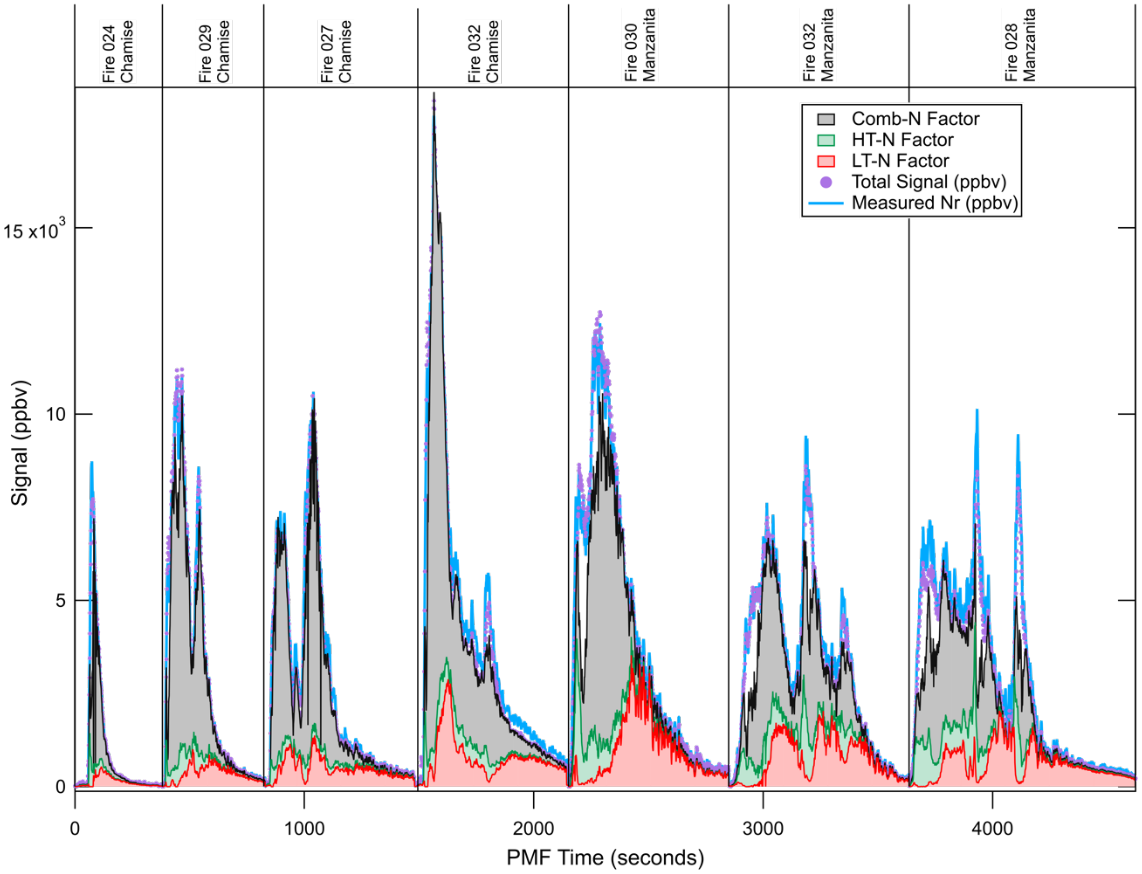

Figure S7. The timeline for the combined PMF analysis of chaparral fuels. The measured N_r is shown as a blue line, the total of N compounds used in the PMF is shown as purple points, and Comb-N (grey), HT-N (green), and LT-N (red) factors plotted stacked on top of one another. The vertical lines show where individual fires start and stop.

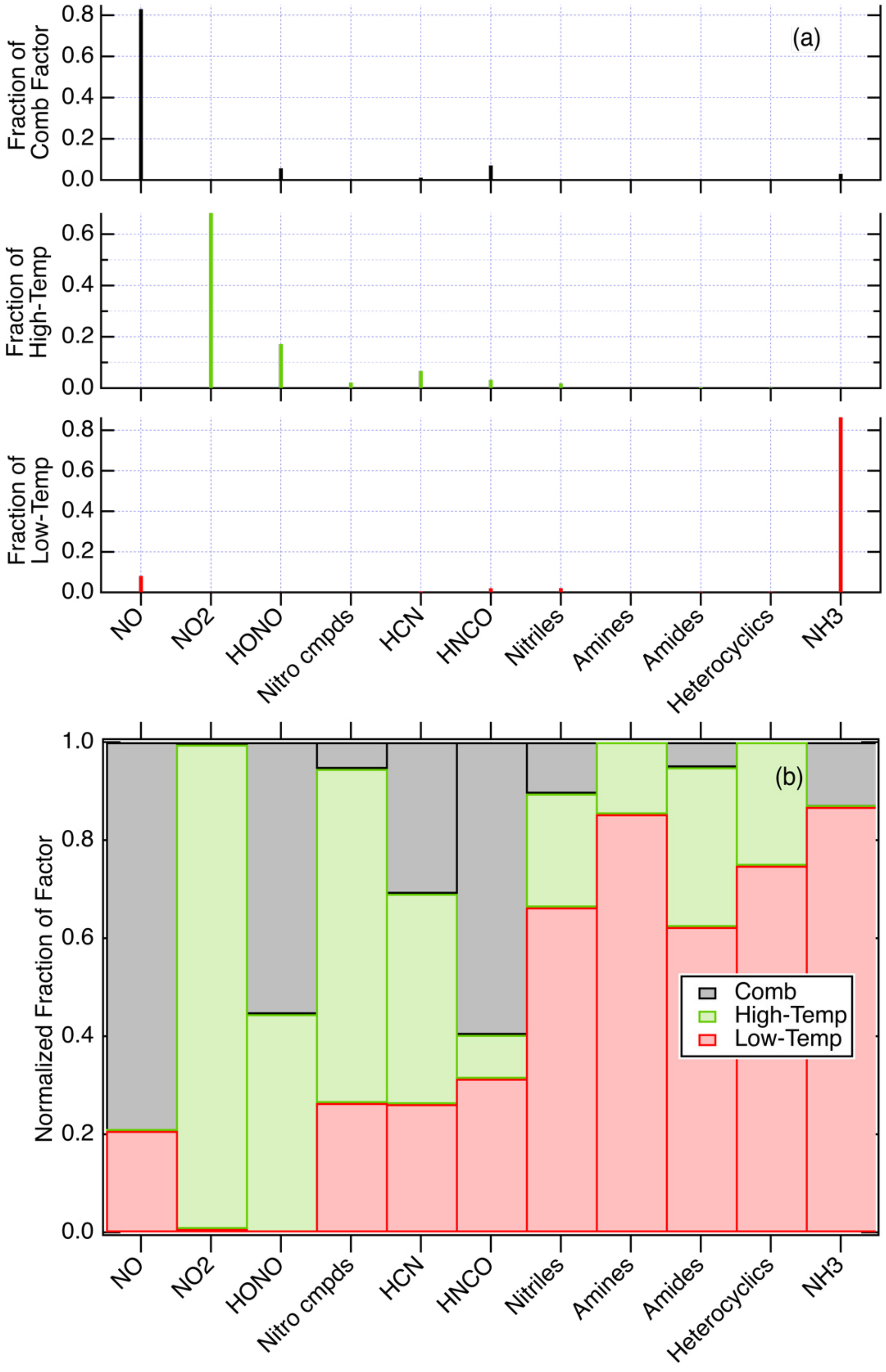

Figure S8. The contributions of nitrogen species to the factors that simulate the emissions from chaparral fuels shown in Figure S7 (panel a), and the fraction of each compound or class found in each factor (panel b).

References:

Karion, A., Sweeney, C., Tans, P., and Newberger, T.: AirCore: An innovative atmospheric sampling system, J. Atmos. Ocean. Technol., 27, 1839-1853, 2010.

Tang, M. J., Cox, R. A., and Kalberer, M.: Compilation and evaluation of gas phase diffusion coefficients of reactive trace gases in the atmosphere: volume 1. Inorganic compounds, Atmos. Chem. Phys., 14, 9233-9247, 2014.