Journal: Atmospheric Chemistry and Physics Title: High- and low-temperature pyrolysis profiles describe volatile organic compound emissions from western US wildfire fuels Author(s): Kanako Sekimoto et al. MS No.: acp-2018-52 MS Type: Research article

Response to Reviewers:

We thank both reviewers for their positive comments and helpful feedback. The manuscript has been revised accordingly. Our responses are written in blue text.

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Reviewer 1

This paper presents results of positive matrix factorization (PMF) analysis on data collected with a Proton Transfer Reaction Mass Spectrometer (PTR-MS) during laboratory burns of various wildfire fuels during the FIREX campaign. The data set, describing VOCs and other volatile components (e.g. NH3), was described in another publication, and here the authors use PMF to show that much of the variability in emission profiles across and within burns can be explained by two factors, which they associated with high- and low-temperature pyrolysis processes. They show that a single pair of factors can explain the variability in most burns nearly as well as fuel/burn-specific factors, with a few exceptions (e.g. rotten wood, duff). They then included a detailed dive into the two factors, including: the absolute and relative contributions of different compounds, function groups represented in each, and their estimated OH reactivities and volatilities. The paper also emphasizes that modified combustion efficiency (MCE), often used to parameterize combustion types and VOC emission profiles, does not capture the pyrolysis-temperature-driven variability captured here, suggesting that it is not a good proxy for varying emission conditions. This is really nice paper, which makes excellent use of this interesting data set to put forward a compelling case for the importance of pyrolysis temperature on dictating the mixture of VOCs emitted from biomass combustion. This is a topic of great interest, as wildfire VOC emissions (and their variability across fires, space and time) are important and poorly constrained inputs for atmospheric models. The analysis is thorough, cutting across a multi-dimensional data set in a logical way, and the paper is clearly written and includes highly informative figures. Therefore, this paper is highly suitable for publication in ACP. Below, I list a number of guestions and minor concerns that I would like to see addressed before the paper's final publication. Most are clarifications, though a number of points are suggestions for additional steps that the authors may wish to take to enhance the impact and usability of their findings in the broader community interested in biomass burning impacts on the atmosphere.

We thank the reviewer for their positive comments. Below we have responded to specific comments.

General comments

Although it was eventually clear, I found the initial attribution of factors to high- and low-temperature pyrolysis processes to be a bit confusing. I think it might be helpful to move Fig. 4b and some more background discussion of combustion processes to the introduction of the paper. There is currently a nice brief introduction (e.g. L60-71), but then the importance of pyrolysis temperature on VOC composition isn't really discussed into well after results are presented (i.e. after discussion of Figs. 1-3). As it is, this feels like a 'grand unveiling' of something that would be better described earlier. For example, line 94 calls high and low-T pyrolysis the 'main processes (sic) of the VOC emissions from biomass burning' without a reference – if this is so, shouldn't that be made clear earlier, with specific references and summary of what is known about VOC emission as a function of pyrolysis temperature outlined early on? This point is also strongly made on Lines 232-234 without much specific justification.

Edits were made in the abstract and introduction to better introduce the relationship between VOC composition and temperature. At line 40, the abstract is revised to read,

"The compositional differences between the two VOC profiles appear to be related to differences in pyrolysis processes of fuel biopolymers at high and low temperatures. These pyrolysis processes are thought to be the main source of VOC emissions."

At line 78, appropriate references are added and the introduction is revised to read,

"The main source of VOC emissions is pyrolysis of the polymers that form biomass such as cellulose, hemicellulose, and lignin. <u>The temperature of the reaction and the physical characteristics of the biopolymer control which pyrolysis mechanism (e.g. depolymerization, fragmentation, or aromatization) is the main source of emitted VOCs (Yokelson et al., 1996; Yokelson et al., 1997; Collard and Blin, 2014; Liu et al., 2016). In a given fire, the processes (i)-(iv) occur simultaneously, but the relative importance of each process and temperature can change with time, which relates to the variability in integrated VOC emissions between different fires."</u>

At line 119, we have revised the introduction to read:

"We show that much of the observed variability in VOCs can be explained by only two factors, <u>and that</u> these two factors are qualitatively related to the temperature of the pyrolysis processes, which are the main sources of the VOC emissions from biomass burning. Based on this result, the two factors are named as a high-temperature pyrolysis factor and a low-temperature pyrolysis factor."

As Figure 4b (temperature diagram from the literature) includes information that is too specific for the Introduction, we decided to leave it in Results and Discussions as is.

Some of the description of VOC quantification is a bit unclear. For example – Line 87 says that 90% of instrument signal could be attributed to identified VOCs, but then on lines 159 and 160 it is stated that 'many ion masses cannot be unambiguously related to a single VOC contributor. . . and cannot be converted to a mixing ratio'. I assume this is because most of the overall signal is due to a relatively small number of compounds, but perhaps this can be clarified a bit – e.g. how many compounds are actually quantified as mixing ratios? Also, can you estimate approximately what fraction of total emitted NMVOC your measurements represent?

At line 205, we have added an example of a detected ion that cannot be unambiguously related to a single VOC. We have also added information about how many compounds were quantified, and what fraction of total VOC emissions this might represent. The insertion is:

"For example, $C_2H_{13}^+$ (m/2 97.101) is a fragmentary product ion of at least five different VOCs, whose relative contributions are different between fires. However, variability in these ion signals still contains information useful for PMF. To interpret the PMF results, we did convert to mixing ratio where possible (Section 2.4). 528 compounds were quantified, of which 156 are identified VOCs. The PTR-ToF-MS measures 50-80% of total emitted non-methane VOC mass, with uncertainty in this value due to semivolatile compounds (Hatch et al., 2017)."

The use of the Pearson's correlation coefficient (r) doesn't really seem appropriate since you are actually presenting regression results (slopes) not correlations alone. Also, the Figure 2 caption states that r was calculated based on log-transformed normalized signals, were slopes also calculated this way? This should be done consistently and described clearly. I'm not an expert statistician, but it seems that there may be a better way to compare factors – as it is, you are using difference in r values be-tween 0.91 and 0.83 (for example) to say that factors are quite similar or quite different (Fig. 2d and 2e). I wonder if there are better ways to contrast the spectra than is presented here?

Both the slope and correlation coefficient were calculated using log-transformed normalized signals. This is now stated clearly in the caption of Figure 2. We looked into other ways of determining correlation coefficients

between the spectra. Pearson's correlation coefficient is the most appropriate correlation coefficient to use here. The use of R^2 does make a better distinction between the spectra that are better correlated (Figure 2 panels a-d) and not as well correlated (Figure 2 panel e), so we have updated Figure 2, Figure S4, Table S1, and the text to use R^2 . Our assessment of correlation is not based on R alone, but also on slope (closer to 1 for the spectra that correlate), and visual inspection of Figure 2 and the other pairs of spectra. Figure 2e shows clearly worse correlation between high-and low-temperature profiles for a single fuel, than between high-temperature (or low-temperature) profiles of different fuels.

As noted in a few places, one of the major drivers for VOC speciation is to understand SOA formation potential, but the final step to that isn't taken. As stated (L 398) yields are an important missing piece here, other similar papers on biomass combustion has taken that step (Bruns et al. 2016, 2017). The authors could consider adding some kind of scoping analysis to this paper, or certainly extending this in future work with this dataset.

SOA yields from the emissions described here were studied during the FIREX campaign. The analysis of this experiment is ongoing and we have now noted that in this section. A reference to Bruns et al. (2016) has also been added. Section 3.3.3 "Volatility" now reads (line 492),

"Oxygenated aromatics have been shown to be important biomass burning SOA precursors (Bruns et al., 2016), and while the SOA yields of many other compounds are unknown, the lower volatility and higher oxygen content of the low-temperature profile suggests a potentially more efficient SOA formation. SOA formation was also studied during the FIREX 2016 campaign, by oxidizing emissions in a chamber, and will be presented separately (Lim et al, in prep, 2018)."

One of the main reasons that MCE appeals as a proxy for combustion conditions is that it is based on easilymeasurable quantities (including from satellites). While you may point out its limits here, it would be great if (relatively) simple alternatives were proposed/discussed. For example, are there any especially robust 'marker species' for the two factors across all fuel/burn types? For example, Cresol and guaiacol seem to be distinct features of high and low T factors with substantial contributions (Fig. 2), but perhaps there are others that are more consistent. Could the ratio of these two serve as a proxy for relative factor strength? How can this approach be simplified to be applied by different analytical approaches or other data sets? Does MCE have any explanatory power for relative factor strength across your data set or in some subsets? Are there any other emission ratios (especially for species that are frequently measured, especially by remote sensing) that do?

We considered several pairs of VOCs that could be used as a proxy for the high vs. low temperature factor strength. Ethyne and furan are a robust pair, although they are not ideal because few instruments other than PTR-MS and GC methods can measure them. We have also added some more discussion of MCE, and an additional figure that shows MCE correlates poorly with factor strength.

At line 545, Section 3.5 has been edited to read and added a new figure (Figure 11),

"However, MCE does not parameterize the relative amounts of high- and low-temperature pyrolysis products very well, <u>either instantaneously or on a fire-integrated basis (Figure 11)</u>."



Figure 11. The comparison of contribution of high-temperature factor versus modified combustion efficiency (MCE). (a) Time series of Fire #37 (Ponderosa pine realistic mixture). (b) Scatter plot of instantaneous high-temperature contribution versus MCE for all Ponderosa pine fires. (c) Scatter plot of fire-integrated high-temperature contribution versus MCE for all fires. Contribution of high-temperature factor was calculated by $JVOC_{high-T} + JVOC_{how-T}$) instantaneously or on a fire-integrated basis.

MCE data in Figure 10 has been removed, and now this figure has only the ratio of fire-integrated VOC molar emissions (see below).



Figure 10. Ratios of fire-integrated molar emissions of total VOCs from high- to low-temperature pyrolysis (" Σ VOC_{High-T}/ Σ VOC_{Low-T}") for different type fuel parts, obtained using PMF results of 15 different fuels.

At line 571 in Section 3.5, additional discussion of ethyne and furan as markers is inserted:

"The relative contributions from the high- and low-temperature processes could be estimated from ratios of distinct marker species that are consistently enhanced in the high and low-temperature profiles. Several such pairs were considered and the ratio of ethyne (C_2H_2) to furan (C_4H_4O) can reasonably predict the ratio of high- to low-temperature emissions as given in Eq. 1:

$$\frac{total VOC, high temperature (ppbv)}{total VOC, low temperature (ppbv)} = \frac{ethyne (ppbv) / 0.0393}{furan (ppbv) / 0.0159}$$
(1)

The derivation and how the ethyne/furan ratio correlates with the high-/low-temperature emission ratio are given in the Supporting Information (S2 and Figure S9). However, this pair is not ideal because measurements of these two species are not frequently available and furan has high reactivity to both O_3 and NO_3 radicals. Future work should assess non-PTR measurements in order to find appropriate external markers."



Figure S9. The comparison of contribution of high-temperature factor versus ethyne/furan ratio. (a) Time series of Fire #37 (Ponderosa pine realistic mixture). (b) Scatter plot of instantaneous high-temperature contribution versus ethyne/furan ratio for all Ponderosa pine fires. (c) Scatter plot of fire-integrated high-temperature contribution versus ethyne/furan ratio for all fires. Contribution of high-temperature factor was calculated by $\int VOC_{high-T} + \int VOC_{how-T}$) instantaneously or on a fire-integrated basis.

The relevant section in the Supporting Information reads:

"S2. Relationship of ethyne:furan ratio to high:low temperature ratio

Trace gases can be used to estimate the emissions from the high/low temperature factors. Here we propose ethyne (C_2H_2) and furan (C_4H_4O) as tracers. Normalized fractions of the high/low temperature factors are 72%/28% for ethyne and 33%/67% for furan. These two compounds have large emissions and low standard deviations in the average emission profiles of 15 different fuels (0.0393 ± 23% ppbv for ethyne in the high-temperature factor and 0.0159 ± 19% ppbv for furan in the low-temperature factor). This reduces to a ratio of approximately:

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\frac{total VOC , high temperature (ppbv)}{total VOC , low temperature (ppbv)} = \frac{ethyne (ppbv) / 0.0393}{furan (ppbv) / 0.0159}
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Average relative error (%) of the ethyne/furan ratio to the total VOC_{High-T}/total VOC_{Low-T} is 50%, except for rotten wood."

(S2)

Specific points:

Lines 239-243 – This point seems like it could use a bit more justification. To my eye, the addition of a third factor in Fig. S2 does seem to make a pretty substantial difference – there is quite a bit of scatter in the fit vs. reconstructed Factor 3 time series plot (bottom right). Is there a way to make this point more convincingly?

According to comments from both reviewers, we have significantly modified Figures S2 and S3 to more clearly show that a two-factor solution is reasonable, and that additional factors do not add useful information.

Figure S2 now shows the mass spectra from the 2-, 3-, and 4- factor solutions. The two factors that account for most of the variability (Factor 1 and Factor 2) do not change substantially as the number of factors increases. The additional factors in the 3- and 4- factor solutions have similar mass spectra to Factor 1 and Factor 2.

Figure S3 now shows the time series of a representative fire of Ponderosa pine. The measured signal is compared to the PMF solution with two, three, and four factors. For each solution (2, 3, and 4-factors), the time series of the individual factors are shown as subplots. In each subplot, the linear best fit of the high- and low-temperature factors is shown. It can now be clearly seen that there is low residual with the 2-factors solution; additional factors do not substantially change the residual; and that each factor from the 3- and 4-factor solutions can be described by a linear combination of the high- and low-temperature factors.



The two new figures are as shown:

Figure S2. Comparison of mass spectra from 2-, 3-, and 4-factor PMF solutions. The two factors that account for most of the variability (Factor 1 and Factor 2) do not change substantially as the number of factors increases. The additional factors in the 3- and 4-factor solutions have similar mass spectra to Factor 1 and Factor 2.



Figure S3. Comparison of time series from 2-, 3-, and 4-factor solutions. The time-series shown is the total instrument signal from a representative fire of Ponderosa Pine (a part of Fire #37). The individual factors are from the PMF analysis of the extended time series (in which all fires of Ponderosa Pine were concatenated). The left-side plots show the stacked contributions of the factors, compared to the measured signal. The small plots on the right show the time series of the individual factors (solid lines). The high- and low-temperature factors were fit to each factor in the 3- and 4-factor solutions. The best-fit was done using the extended time series. These best-fits are shown as the shaded areas in the right-side plots, and the best-fit equation and correlation coefficient are also provided.

Line 337-339 – This is a bit confusing/misleading – pyrolysis will still happen during flaming combustion as there is heat transfer from the flame to surrounding biomass. As you state elsewhere, all of these processes are happening simultaneously in most cases. Therefore, it might be expected that the dominance of different factors might be linked to flaming- versus smoldering-dominated burns or stages of a burn.

At the end of Section 3.2 (line 424), the description has been revised to read,

"The present analysis predominantly focuses on VOCs. The VOC emissions from biomass burning are dominated by pyrolysis reactions of biopolymers. However, **not all species are emitted from pyrolysis** reactions. For example, flaming combustion releases CO₂, NO_x, HONO, and black carbon, etc. This is a separate process and cannot be expected to be captured by our VOC framework. In section 3.5 we show that MCE, which delineates flaming versus smoldering combustion, is a poorer descriptor of VOC variability than the high versus low-temperature pyrolysis framework."

We also added the following figure as Figure S6 in the Supporting Information, in order to show that the emissions of compounds originating from flaming combustion (i.e., CO_2 and NO_x) do not correlate with the high-and low-temperature pyrolysis factors.



Figure S6. Linear fits of (a) CO_2 , (b) NO_x , and (c) CO emissions (in ppmv) by the high- and low-temperature pyrolysis time series (in ncps) for Fire #37 (Ponderosa pine realistic mixture). Each plot shows the stacked contributions of the high- and low-temperature factors (shaded area), compared to the measured mixing ratios (solid line). The best-fit equation and correlation coefficient are also provided.

Line 232 - should be 'make a higher contribution in the low-T factor', I think?

Line 373 has been clarified to read,

"<u>Emissions</u> of these compounds have a <u>larger</u> contribution from the low-temperature factor ($F_{low-T} = 60-100\%$)."

Line 391-392 – This doesn't seem necessary considering that your estimated OH reactivities for the two factors are basically identical. This is a nice result, that suggests that OH reactivity scales directly with NMVOC (for the compounds you've detected). Seems like something to note.

At line 484, this sentence has been revised to read,

"Since the total VOC emissions in real-world fires come from a mixture of the high- and low- temperature pyrolysis factors, the total OH reactivity of fresh emissions should scale directly with VOC concentration."

Section 3.3.3 – It would seem more appropriate to show this distribution on a mass (versus molar) basis, as is typically done for volatility basis set representations. As noted above, yields could be approximated to take the next step, which would be very helpful but not necessary.





Line 445 -450 – I see this is true across fuel/burn types, but what about within a burn? Are there any stages in which transitions in MCE map to transitions in factor-strength? The time-series discussed here shows CO/CO2 for the rotten pine case (Fig. S6), but that doesn't seem like an appropriate example as it is pretty much

dominated by the low-T factor (I can't visually average these two. . .). Having some time series plots with MCE during a burn along with the factor contributions (possibly a separate trace on Fig. 1) would address this better. Is there any correlation between MCE and the relative contribution from the different factors during burns?

MCE does not parameterize the relative amounts of high- and low-temperature pyrolysis products very well, either instantaneously or on a fire-integrated basis. This is because emissions of CO_2 (and NO_x) from flaming combustion do not correlate with a linear combination of the high- and low-temperature pyrolysis processes, as shown in "Figure S6" newly added (please see above).

According to comments from both reviewers, we have also added some more discussion of MCE, and an additional figure that shows MCE correlates poorly with factor strength. Section 3.5 has been edited to read (line 545) and added a new figure (Figure 11),

"However, MCE does not parameterize the relative amounts of high- and low-temperature pyrolysis products very well, either instantaneously or on a fire-integrated basis (Figure 11)."

The new Figure 11 is shown in our response to the general comments from this reviewer.

According to the reviewer's comment, we added the time series of CO_2 , CO, NO_x , and MCE in Figure 1; also, the corresponding sentences in Section 3.1. have been revised to read (line 285),

"On the contrary, emissions of compounds mainly from flaming or non-pyrolysis smoldering processes, such as CO, CO_2 , and NO_x (Figure 1c), do not correlate well with the individual PMF factors (more detailed discussion is given in Section 3.5). This indicates that the two PMF factors do not correspond to the flaming and smoldering combustion processes that are described by MCE and often referenced in biomass burning literature. The main source of VOC emissions is pyrolysis of fuel biopolymers, and *not* the flaming and/or other combustion processes."

The revised Figure 1 is as follows:



Figure 1. Results for an example burn of Ponderosa pine realistic mixture (Fire #37). (a) Time series of ion signals of 574 ion peaks, naphthalene ($C_{10}H_8 \cdot H^+$, m/z 129.070), and syringol ($C_8H_{10}O_3 \cdot H^+$, m/z 155.070). (b) PMF results of 2-factor solution. The grey and pink colors are stacked, not overlapped. (c) Time series of mixing ratios of CO₂, CO, and NO_x measured by open-path Fourier transform infrared (OP-FTIR) optical spectroscopy and the modified combustion efficiency (MCE) (Selimovic et al., 2018). The MCE trace is colored by the key and scale on the right.

Line 558-560- Residuals from PMF fitting are not really discussed elsewhere in the paper. They either should be or the effectiveness of fitting discussed in another way here.

Residuals from PMF are discussed in Section 3.1. We have clarified this through some minor edits in Section 3.1 (line 279):

"These two PMF factors (Figure 1b) describe the total VOC emissions remarkably well for most fuels: <u>residuals</u> (the differences between the measured ion signals and the calculated ion signals based on the PMF fits) are less than 15% on average, <u>except for Douglas fir, Engelmann spruce, and Subalpine fir for which the residual</u> <u>average is 20-25%. The residuals for individual fuels are summarized in</u> Table 1c." The residuals from Duff were higher. This was mentioned at the end of Section 3.1 and discussed in detail in Section 3.6.2. The quantitative measure of effectiveness of fitting, "Q" is expressed by summation of squared scaled residuals for each experimental data point and is discussed in detail in S1.2.

Figure 4b – Would like a more detailed caption. What do color bars correspond to - just temperature ranges? Why does the red bar span a wider temperature range for lignin?

The color bars correspond to temperature ranges reported in the literature (Collard and Blin, 2014). According to the reviewer's comment, a more detailed caption was added to Figure 4, and now reads,

"Figure 4. (a) Normalized fraction of factors for selected biomass pyrolysis products, obtained using PMF results of 15 different fuels. (b) Diagram of the relationship between pyrolysis temperature and products for hemicellulose, cellulose, and lignin, <u>as reported in the literature (Collard and Blin, 2014). Individual color bars</u> show the temperature range to form specific products described by chemical structures."

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Reviewer 2

General Comments:

The paper by Sekimoto et al. seeks to understand the "instantaneous" variability in VOC emissions from biomass burning, to develop predictive capability of the emissions. The authors report that a PMF solution consisting of just two emission profile factors can explain on average 85% of the VOC emissions across various fuels representative of the western US. They state that the profiles are remarkably similar across almost all of the fuel types tested. According to the authors, the two factor solution from the PMF model could be attributed to "high-temperature" and "low-temperature" pyrolysis processes. They suggest that this type of temperature based parameterization of emissions could be widely useful to model VOC emissions from many types of biomass burning in the western US, with exceptions such as burns of duff and rotten wood. Certainly this is a very interesting topic and the idea of being able to predict emissions resulting from complex combustion chemistry using temperature regimes is indeed appealing. As an idea I do find the paper novel. However, there appear to be major shortcomings in the current version of the paper and analyses. Thus, I was not able to conclude that the evidence presented in the paper is sufficient and convincing to have confidence in the main take home message of the paper that has been aptly summarized in its title, namely: "High- and low-temperature pyrolysis profiles describe volatile organic compound emissions from western US wildfire fuels"

We thank the reviewer for their positive comments, and hope we have sufficiently addressed their reservations in the following response. Overall, we stress that we do not claim to have developed a quantitative temperaturebased parameterization that can predict VOC emissions in any scenario. To clarify this, we have edited sections of the abstract, introduction, and other parts of the paper. The edits are intended to more clearly convey the major points of this paper:

- (1) We have determined that there are two distinct emission profiles. These can describe most VOC compositional variability.
- (2) We have evidence that strongly suggests the profiles have a physically realistic explanation (temperature of the pyrolysis process).
- (3) Because the two profiles are likely derived from processes that occur in a wide variety of fires, this conceptual view of VOC emissions could be useful beyond this laboratory study.

Specifically, we have added discussion and a figure (now Figure 11) showing that MCE has limitations to describe VOC compositional variability, supplemental figures (Figures S2 and S3) that better support the choice of a two-factor PMF solution, and edits so as not to suggest that we have a fully-quantitative temperature-based parameterization.

Edits to the abstract and introduction are listed here. Edits in other sections of the paper are listed below the reviewer specific concerns.

At line 40, the abstract has been edited to read,

"The compositional differences between the two VOC profiles appear to be related to differences in pyrolysis processes of fuel biopolymers at high and low temperatures. These pyrolysis processes are thought to be the main source of VOC emissions."

The last sentence of the abstract has been moved to the conclusions (line 725):

"With this further work, the VOC profiles could be widely useful to model VOC emissions from many types of biomass burning in the western US, with additions to the framework being needed for fires that burn a lot of duff."

At line 106, the last paragraph of the introduction now states,

"The aims of this work are to understand the variation in gas-phase emissions both over the course of a fire and on a fire-integrated basis. <u>Ultimately, this improved understanding of emissions variability could be used</u> to simplify predictions of the emission of secondary organic aerosol (SOA) and ozone precursors."

Major reservations and concerns:

1) The present analyses and discussion completely omits the role of oxygen (read air to fuel ratio) during the combustion experiments. I find it illogical that burn conditions such as the oxygen supply when the fuel is being burnt can be completely discounted from playing any role. The major advantage of the modified combustion efficiency (MCE) developed by some of the senior authors in their previous works is that it is able to capture the role of oxygen availability between smoldering and flaming dominated combustion conditions and experimental evidence in the form of the delta CO/delta CO2 ratios helps us reconcile it with the real world process of the overall oxidation of the carbon in the fuel (e.g. incomplete oxidation implies more CO and reduced carbon compounds will be emitted). Though the authors show in Fig 10, that the ratio of high temperature to low temperature emissions shows poor dependency on the MCE, it would have been more convincing to show this using the online real time data of the burns. For example, the authors could add the time series data of CO and CO2 for the same fire as additional panels to Figure 1. This would help distinguish whether the new terminology of high and low temperature pyrolysis are simply a variant of the older terminology of flaming and smoldering fire stages. To put it another way, will the high/low temperature burn emissions of the fuel under low and high oxygen conditions show similar profiles and behavior? Knowing the important role played by oxygen in flame chemistry, how can such an important aspect be ignored from the parameterization? If the authors think otherwise, then some experimental data in support of their contention is certainly warranted else one cannot accept the parameterization proposed by the authors as generically as they suggest.

First we clarify a misunderstanding. There is no evidence of oxygen depletion at low MCE or high CO/CO2 (see Akagi et al 2011). In open biomass burning the air can rush in and supply plenty of O2. Low MCE indicates that the amount of pyrolysis or glowing products are high compared to flaming products (Yokelson et al., 1996), which can happen for a variety of reasons, but often related to fuel geometry. PMF examines the pyrolysis products in more detail than is possible with MCE alone. Flaming chemistry was not studied in this paper.

From this comment, we understand that the reviewer would like to know if the instantaneous MCE has any correlation to the relative intensity of the high- and low-temperature profiles (1). The reviewer also is curious how specific burn conditions quantitatively affect the ratio between the two profiles, and whether the high- / low-temperature description accounts for variation in burn conditions (2). Finally, the reviewer is understandably hesitant to move away from MCE as a descriptor of emissions variability because the connection between the experimental measure of MCE (delta CO/delta CO_2) and the fire characteristic it describes (flaming vs. smoldering) is grounded in a well-understood physical process (oxidation extent of the fuel) (3).

(1) We first show more clearly that MCE is a poor predictor of the high- / low-temperature factor balance. Both reviewers requested this.

First, we have edited Figure 1 as the reviewer suggested. There is now a third panel that shows the time series of CO, CO_2 , NO_x , and MCE for an example fire. We changed the example fire from Fire #02 (ponderosa pine, realistic mixture) to Fire #37 (also ponderosa pine, realistic mixture) because there was incomplete CO, CO_2 , and NO_x data for Fire #02.



Figure 1. Results for an example burn of Ponderosa pine realistic mixture (Fire #37). (a) Time series of ion signals of 574 ion peaks, naphthalene ($C_{10}H_8 \cdot H^+$, m/z 129.070), and syringol ($C_8H_{10}O_3 \cdot H^+$, m/z 155.070). (b) PMF results of 2-factor solution. The grey and pink colors are stacked, not overlapped. (c) Time series of mixing ratios of CO₂, CO, and NO_x measured by open-path Fourier transform infrared (OP-FTIR) optical spectroscopy and the modified combustion efficiency (MCE) (Selimovic et al., 2018). The MCE trace is colored by the key and scale on the right.

Second, we added a Figure S6 to the supplemental material. This figure shows a linear best-fit of the High-temperature and low-temperature time series to the time series of CO_2 , NO_x , and CO. Flaming-combustion compounds CO2 and NOx clearly have a weak relationship to the high- and low-temperature factors. In section 3.1 (line 285), we have added

"On the contrary, emissions of compounds mainly from flaming or non-pyrolysis smoldering processes, such as CO, CO_2 , and NO_x (Figure 1c), do not correlate well with the individual PMF factors (more detailed discussion is given in Section 3.5). This indicates that the two PMF factors do not correspond to the

flaming and smoldering combustion processes that are described by MCE and often referenced in biomass burning literature. The main source of VOC emissions is pyrolysis of fuel biopolymers, and *not* the flaming and/or other combustion processes. Therefore, we primarily attribute these two factors to hightemperature pyrolysis and low-temperature pyrolysis, respectively, and will use these names to describe these factors in this work."



Figure S6. Linear fits of (a) CO_2 , (b) NO_x , and (c) CO emissions (in ppmv) by the high- and low-temperature pyrolysis time series (in ncps) for Fire #37 (Ponderosa pine realistic mixture). Each plot shows the stacked contributions of the high- and low-temperature factors (shaded area), compared to the measured mixing ratios (solid line). The best-fit equation and correlation coefficient are also provided.

Third, Section 3.5 has been edited and added a new figure (Figure 11). This new figure includes a time-series of MCE and high/low-temperature factors for an example fire; a comparison of instantaneous MCE to high/low-temperature factors across many fires; and a comparison of fire-integrated MCE to high/low-temperature factors across all fires.

The edit reads, "However, MCE does not parameterize the relative amounts of high- and low-temperature pyrolysis products very well, <u>either instantaneously or on a fire-integrated basis (Figure 11)</u>." (line 545) MCE data in Figure 10 has been removed, and now this figure has only the ratio of fire-integrated VOC molar emissions.



Figure 11. The comparison of contribution of high-temperature factor versus modified combustion efficiency (MCE). (a) Time series of Fire #37 (Ponderosa pine realistic mixture). (b) Scatter plot of instantaneous high-temperature contribution versus MCE for all Ponderosa pine fires. (c) Scatter plot of fire-integrated high-temperature contribution versus MCE for all fires. Contribution of high-temperature factor was calculated by $\Sigma VOC_{high-T} + \Sigma VOC_{low-T}$) instantaneously or on a fire-integrated basis.

(2) Next, we address whether the high- / low-temperature description accounts for variation in burn conditions, and how specific burn conditions may quantitatively affect the ratio between the two profiles. One of the strengths of PMF analysis is that we do not need to know all the details of all the processes going on in a fire: PMF groups together all the processes that result in similar VOC emission profiles. A wide range of MCE occurred during the Firelab experiments (newly added Figure 11, Table 1). Because the two PMF profiles describe 85% of variability across all fires, then the two PMF profiles captured the role of various influences as described below.

We did not attempt to develop a quantitative parameterization of the ratio of high-temperature factor to lowtemperature factor based on specific fuel conditions (moisture content, surface area, and so on). Such a parameterization is well beyond the scope of this manuscript, but could be a useful target for future work. The fires studied in this experiment incorporated a wide range of fuel moisture content and MCE, so we may reasonably suggest that the high- and low-temperature description of emissions may be applicable under many conditions. We have shown this first by including the fuel moisture content and MCE information in Table 1, which is now in the main text, and by stating the range of moisture content and MCE in section 2.2 (line 168): "Fuel moisture content ranged from 0.6% to 55.6%, and instantaneous MCE ranged from 0.75 to 1." We edited section 3.2 (line 388) to read,

"These many diverse chemical processes are likely happening simultaneously during a fire, and their relative intensities may change based on fuel composition, fuel moisture content, or other as-yet poorly defined parameters. However, the net result of all these variables is the emission of just two major compositional groups. The VOCs that comprise these two groups mostly consist of the pyrolysis products described above and their analogs. During most of these fires, the emissions of any particular VOC can be described by a linear combination of the high-temperature and low-temperature pyrolysis time series." We edited the last paragraph in section 3.5 (line 600) to read,

"The current study incorporated a wide range of MCEs and fuel moisture contents (Table 1), so the twofactor description may be applicable under many conditions. However, some other factors should be required for specific burns, as discussed below."

(3) Finally, we discuss the relationship between the two PMF-derived profiles and physical processes known to occur in fires. The high-/low-temperature description is analogous to MCE in several ways. MCE describes the overall degree of carbon oxidation; similarly, the high-/low-temperature profiles describe the overall pyrolysis temperature. MCE is experimentally measured by the ratio of CO and CO₂, and the high- and low-temperature profiles are measured by the VOC composition. The CO and CO₂ ratio is related to the extent of carbon oxidation because less efficient flame-processing results in a relative enhancement of reduced compounds. Similarly, the VOC composition is related to the pyrolysis temperature because higher temperatures enable bond-breaking in biopolymers, leading to smaller molecules at higher temperatures and larger, more substituted molecules at lower temperatures. The relationship between temperature and VOC composition is well established in pyrolysis literature (e.g. Collard and Blin, 2014, Liu et al., 2016). We have edited several sections of the text to clarify.

We have edited section 3.2 (line 339) to read,

"The compositional differences between the two profiles can be qualitatively explained by the temperature of the pyrolysis reactions thought to be the main production mechanism of the VOCs, such as depolymerization, fragmentation, and aromatization (Yokelson et al., 1996; Yokelson et al., 1997; Collard and Blin, 2014; Liu et al., 2016). This is illustrated by the relative contributions from the high-temperature versus low-temperature factors for most emitted VOCs. VOCs expected from high-temperature processes have a higher emissions contribution from the high-temperature factor, and likewise for low-temperature VOCs and the low-temperature factor."

In section 3.5 (line 557), we have added,

"Our results indicate that VOC emissions are even more closely correlated to the biopolymer composition and the surface-to-volume ratios of fuels, than to the MCE."

Additional material has been added to Section 3.5 describing the correlation between low- and high-temperature factors and the measured air temperature, and this is detailed in our response to reviewer comment #3.

2) The justification for the two factor PMF solution is not at all clear. Figure 3 should be modified to show the average VOC emission profiles of both the high temperature and low temperature factor for a PMF solution of 2 factors, 3 factors and 4 factors respectively, in the same panel (as three different colored lines for each m/z). In addition, the same should also be shown for the third and fourth factors. The issue with the correlation plots given in the supplement is that they mask more than they reveal whereas in a VOC emission profile of the type shown in Fig 3, specific information on which compounds migrate from one factor to a new factor can be clearly made out and is more helpful for assessing whether the proposed solution is justified.

According to comments from both reviewers, we have significantly modified Figures S2 and S3 to more clearly show that a two-factor solution is reasonable, and that additional factors do not add useful information.



Figure S2 now shows the mass spectra from the 2-, 3-, and 4- factor solutions. The two factors that account for most of the variability (Factor 1 and Factor 2) do not change substantially as the number of factors increases. The additional factors in the 3- and 4- factor solutions have similar mass spectra to Factor 1 and Factor 2.

Figure S2. Comparison of mass spectra from 2-, 3-, and 4-factor PMF solutions. The two factors that account for most of the variability (Factor 1 and Factor 2) do not change substantially as the number of factors increases. The additional factors in the 3- and 4-factor solutions have similar mass spectra to Factor 1 and Factor 2.

Figure S3 now shows the time series of a representative fire of Ponderosa pine. The measured signal is compared to the PMF solution with two, three, and four factors. For each solution (2, 3, and 4-factors), the time series of the individual factors are shown as subplots. In each subplot, the linear best fit of the high- and low-temperature factors is shown. It can now be clearly seen that there is low residual with the 2-factors solution; additional factors do not substantially change the residual; and that each factor from the 3- and 4-factor solutions can be described by a linear combination of the high- and low-temperature factors.



Figure S3. Comparison of time series from 2-, 3-, and 4-factor solutions. The time-series shown is the total instrument signal from a representative fire of Ponderosa Pine (a part of Fire #37). The individual factors are from the PMF analysis of the extended time series (in which all fires of Ponderosa Pine were concatenated). The left-side plots show the stacked contributions of the factors, compared to the measured signal. The small plots on the right show the time series of the individual factors (solid lines). The high- and low-temperature factors were fit to each factor in the 3- and 4-factor solutions. The best-fit was done using the extended time series. These best-fits are shown as the shaded areas in the right-side plots, and the best-fit equation and correlation coefficient are also provided.

3) The paper makes generic assertions about low and high temperature emissions, but in none of the experiments was the temperature data provided/shown or even mentioned. I presume the authors have such data /or can provide it. While I understand different parts of the fuel may be subject to different stages of combustion (flaming, combustion, distillation) at the same time and the emissions are a net resultant of these, some temperature data from the burn experiments where a large temperature range was observed from start to finish is certainly in order.

Temperature data was taken during the experiment, via the air temperature of the emissions at the level of the sampling inlet (data from FTIR instrument). The temperature of the fire itself is not easy to define or measure. A thermometer placed inside the fire will only measure the local temperature. An external measurement such as an IR camera may not detect interior parts of the fire that are hidden from view. The air temperature measurement was not always related to the fire conditions because it is strongly affected by the amount of fuel burning relative to the amount of dilution air, the background temperature changed considerably between fires and over the course of a fire, and there was frequently a lag between the onset of emissions and air temperature increase. We have now included a supplementary figure (S8) showing some of this data, for Ponderosa pine fires. There is some correlation between air temperature and the VOC factors. For other fires, the relationship is not clear, likely due to the aforementioned issues with the temperature measurement. Therefore we do not rely on this data to quantitatively parameterize the high- and low-temperature factors.



Figure S8. The comparison of contribution of high-temperature factor versus air temperature of the emissions measured at the sampling inlet of the PTR-ToF-MS. (a) Time series of Fire #37 (Ponderosa pine realistic mixture). (b)-(d) Scatter plots of instantaneous high-temperature contribution versus temperature for Fire #37, #59 (Ponderosa pine realistic mixture), and #38 (Ponderosa pine litter).

At line 559, Section 3.5 has been edited to read,

"It is also seen that for some fires the air temperature correlates with the high-temperature contribution (e.g., Fires #37 and #59 shown in Figure S8a-c). This suggests that the VOC emissions are certainly related to the temperature within a fire. However, some other burns did not have a good correlation between the temperature and VOC emissions (e.g., Fire #38 shown in Figure S8d), because the temperature measurement had some issues in the present work: (i) background temperature for each burn was different, (ii) some burns have colder temperature at end compared to start, which means that the laboratory was not controlled at constant temperature, and (iii) the increase in air temperature often lagged behind the emissions, especially at the start of a fire."

In Section 2.2 (line 172), we have added:

"The present experiments did not have a direct measurement of temperature within the fire, which is not homogeneous and therefore difficult to define. Rather, the air temperature of the emissions was measured by the FTIR instrument, located at the sampling inlet of the PTR-ToF-MS. The hot gases from the fire were mixed with air from the room, cooling the air significantly, but the trends in temperature are related to the initial temperature of the emitted gases."

4) The authors should clarify/mention the practical steps that need to be followed to employ the high and low temperature pyrolysis profiles for modeling VOC emissions from "many types of biomass burning" as asserted in the abstract and conclusion.

At line 719, the Conclusions section was revised as follows:

"Our framework provides a way to understand VOC emissions variability in other laboratory and field studies of biomass burning. We highlight two areas of useful future work. First, external tracers should be found that will allow the prediction of the relative contribution of individual profiles. This could include specific chemical species, an understanding of how fuel or burn characteristics relate to the relative contribution of the two profiles, or a relationship between some measure of fire temperature and the VOC profiles. Second, the SOA and ozone formation potential of the two profiles should be determined. With this further work, the VOC profiles could be widely useful to model VOC emissions from many types of biomass burning in the western US, with additions to the framework being needed for fires that burn a lot of duff."

Some specific details:

Line 136-138: Citing Selimovic et al. 2017 for important and relevant details is not sufficient in my opinion. For this paper to be considered as an independent paper, at least a summary of the essential info needs to be provided in the main text. For example, how many fires for each fuel type were sampled in the present work? how similar / dissimilar were the emission profiles when the same fuel type was burnt? Was the pyrolysis temperature or temperature profile during the burns measured? What about the variability induced by other burn conditions?

Table S1, which contains a summary of the fuels burned, which fuel components were burned in each fire, the number of fires of each type, the residuals from PMF, and correlation coefficients of the emission profiles, has been added to the main text in section 2.2 "Fuel and biomass burn descriptions" as Table 1. Additionally, we added MCE and fuel moisture content information to this table. The lines 168-177 have been edited to read,

"Fuel moisture content ranged from 0.6% to 55.6%, and instantaneous MCE ranged from 0.75 to 1. Additional details on the fires and fuels are given by Selimovic et al. (2018) including: pre- and post-fire weight, weight of fuel components, and elemental composition (C, H, N, S, and Cl by weight). Each fuel type was burned several times. All fires consumed most of the fuel. The present experiments did not have a direct measurement of temperature within the fire, which is not homogeneous and therefore difficult to define. Rather, the air temperature of the emissions was measured by the FTIR instrument, located at the sampling inlet of the PTR-ToF-MS. The hot gases from the fire were mixed with air from the room, cooling the air significantly, but the trends in temperature are related to the initial temperature of the emitted gases."

Table1. (a) Data numbers and corresponding details of 15 different fuels used in PMF analysis. (b) Average MCE and fuel moisture content. (c) Residuals of 2-factor PMF solutions. (d) Correlation with average VOC emission profile (Figure 3).

Engl	(a) Data number for consolidated PMF					(b) Eins also materializa (c) Devidual 10/13		(d) Correlation with average VOC emission profile (Figure 3)			
ruei		(a) Data number for consolidated PMP			(b) Fire characteristics		(c) Residual [%]	High-tem	perature pyrolysis factor	Low-temperature pyrolysis factor	
	Total	Detail			MCE	Moiture content	Average ± STDV (maximum, minimum)	Slope	Correlation coefficient (r ²)	Slope	Correlation coefficient (r ²)
		Realistic	5	(Fire 01, 02, 37, 59, 72)	0.913-0.940	24.3-31.8%					
1 Pondorora nino	10	Canopy	2	(Fire 19, 39)	0.904-0.935	5 40.4-51.1%	157+76(289,77)	$\textbf{0.976} \pm \textbf{0.004}$	0.9393	1.012 ± 0.005	0.9245
1. ronuerosa pine	10	Litter	1	(Fire 38)	0.945	5 6.2%	13.7 ± 7.6 (26.9, 7.7)				
		Rotten log	2	(Fire 13, 73)	0.932-0.95	2.9-5.7%					
		Realistic	4	(Fire 06, 07, 58, 63)	0.927-0.943	3 20.3-24.4%					
2. Lodgepole pine	7	Canopy	1	(Fire 40)	0.924	49.30%	14.8 ± 4.9 (23.3, 10.9)	0.990 ± 0.004	0.9586	0.990 ± 0.002	0.9716
		Litter	2	(Fire 21, 41)	0.925-0.938	3 7.0-10.5%					
3. Loblolly pine	2	Litter	2	(Fire 35, 53)	0.922-0.929	5.4-10.9%	6.3 ± 0.3 (6.6, 6.1)	0.989 ± 0.007	0.8662	0.960 ± 0.004	0.8862
		Realistic	2	(Fire 14, 57)	0.926-0.951	23.3-25.7%					
4. Douglas fir	4	Canopy	1	(Fire 18)	0.928	3 50.3%	21.2 ± 9.3 (34.9, 14.9)	0.996 ± 0.004	0.9508	0.999 ± 0.003	0.9563
		Litter	1	(Fire 43)	0.951	3.0%					
		Realistic	1	(Fire 08)	0.920	13.0%	20 5 + 2 4 (22 2 18 8) ^b	0 999 + 0 006 b	0 9019 b	0 960 + 0 004 5	0 9004 ^b
5. Engelmann spruce	3	Canopy	1	(Fire 25)	0.950	34.0%	20.5 ± 2.4 (22.2, 10.8)	0.555 ± 0.000	0.7017	0.900 ± 0.004	0.9004
		Duff	1	(Fire 26)	0.81	0.6%	82.0	-	-	-	-
		Realistic	2	(Fire 47, 67)	0.932-0.942	32.8-35.6%		1.001 ± 0.005 ^b	0.9359 ^b	$0.999 \pm 0.003^{\ b}$	0.9547 ^b
6. Subalnine fir	6	Canopy	2	(Fire 15, 23)	0.886-0.947	17.6-55.5%	23.0 ± 14.1 (45.2, 9.1) ^b				
		Litter	1	(Fire 51)	0.900	6.6%					
		Duff	1	(Fire 56)	0.880	6 0.9%	87.0		-		-
7. Juniper	2	Canopy	2	(Fire 68, 75)	0.928-0.939	45.0-48.0%	6.4 ± 3.0 (8.5, 4.3)	1.016 ± 0.006	0.8872	0.971 ± 0.004	0.9010
8. Bear grass	1	-		(Fire 62)	0.89	55.1%	5.6	1.039 ± 0.006	0.8847	1.006 ± 0.004	0.9174
9. Excelsior	2	-		(Fire 49, 61)	0.945-0.97	3.9-5.4%	6.2 ± 3.0 (8.3, 4.0)	1.04 ± 0.01	0.6806	1.012 ± 0.007	0.8521
10. Ceatnothus	2	Shrub	2	(Fire 69, 74)	0.942-0.94	17.7-27.9%	10.2 ± 1.1 (11.0, 9.5)	1.000 ± 0.007	0.8416	1.030 ± 0.006	0.8985
11. Chamise (contaminated)	3	Canopy	3	(Fire 24, 29, 46)	0.948-0.959	0 10.9-16.1%	13.1 ± 3.9 (16.0, 8.6)	1.037 ± 0.006	0.8951	1.044 ± 0.004	0.9477
12. Chamise (uncontaminated)	3	Canopy	3	(Fire 27, 32, 48)	0.946-0.954	6.2-17.1%	12.6 ± 2.0 (14.2, 10.4)	1.017 ± 0.005	0.9322	1.024 ± 0.004	0.9299
13. Manzanita (contaminated)	2	Canopy	2	(Fire 30, 33)	0.962-0.963	3 23.5-26.7%	13.0 ± 1.1 (13.8, 12.3)	$\textbf{0.997} \pm \textbf{0.004}$	0.9347	1.034 ± 0.004	0.9504
14. Manzanita (uncontaminated)	2	Canopy	2	(Fire 28, 34)	0.963-0.964	25.7-26.3%	7.3 ± 1.1 (8.0, 6.5)	1.015 ± 0.005	0.9229	1.043 ± 0.005	0.9224
15. Sagebrush	2	Shrub	2	(Fire 66, 71)	0.919-0.922	37.8-54.2%	7.0 ± 2.1 (8.5, 5.6)	0.993 ± 0.005	0.9046	1.011 ± 0.004	0.9306

* Residual [%] = [Total measured ion signal - Total synthetic ion signal of high- and low-temperature factors] / Total measured ion signal x 100 b "Duff" data is excluded.

Further discussion points:

The authors need to elaborate and clarify regarding the limitations of their methodology. In particular, is the interpretation of the data resting just on the statistical treatment, correlation with known products emitted at certain stages of combustion and a hypothesized area/volume ratio? If so, how can these findings be extrapolated to scenarios in the real world which differ from the experimental conditions of the present work? How would other known factors which are missing from their interpretation and analyses such as oxygen (air to fuel ratio variability) and/or moisture content complicate or change the predicted emission behavior? In particular, if emissions resulting from burns of duff and rotten wood are not explained well by their present predictive algorithm, could variability of conditions significantly alter VOC emission profiles of the other currently "well explained" fuels.

To answer this comment, we have added additional information and discussion comparing the range of fire conditions in this study and those reported in the literature, and have elaborated necessary future work and the limitations of this study. The specific edits are as follows.

The third paragraph of Section 3.5 has been edited with additional information (MCE) for the previous field and laboratory studies, in order to show that the field (and previous laboratory) data have large variability in burn conditions:

"Studies of laboratory burns and wildfires have reported variable emission ratios (or factors) for various VOCs as well as fire-integrated MCE, even for similar fuel types. Here we investigate how well total VOC emissions in biomass burning can be fit by the average VOC emission profiles (Figure 3) using emission factors and ratios reported in the literature for laboratory and field burns (Gilman et al., 2015; Stockwell et al., 2015; Akagi et al., 2011). When fitting the present high- and low-temperature factors to the other biomass burning data, total VOC emissions can be described with different relative fractions of the factors (Figure S10). For example, the best fit to a laboratory study by Gilman et al. (2015), using fuels from southwestern, southeastern, and northern U.S. (e.g., pine, spruce, fir, chaparral, mesquite, and oak) with MCE = 0.75-0.98, includes 32% hightemperature and 68% low-temperature VOC emissions; for another laboratory study by Stockwell et al. (2015) including several types of grass, spruce, and chaparral with MCE = 0.68-0.99, 59% high temperature and 41% low temperature; temperate forest fires (MCE = 0.95) reported by Akagi et al. (2011), 77% high temperature and 23% low temperature, while in the case of chaparral fires (MCE = 0.96), 48% high temperature and 52% low temperature. The fitting can be done with high correlation coefficient ($r \ge 0.92$) for all the literature data (Figure S10). This is further evidence that at most two factors can explain the majority of VOC variability. Therefore, these two factors could be used to fill in VOCs not measured in the other studies which sometimes had less chemical detail. The current study incorporated a wide range of MCE and fuel moisture content

(Table 1), so the two-factor description may be applicable under many conditions. However, some other factors should be required for specific burns, as discussed below."

The Conclusions section was revised to elaborate on future work as follows (noted previously in response to comment #4):

"Our framework provides a way to understand VOC emissions variability in other laboratory and field studies of biomass burning. We highlight two areas of useful future work. First, external tracers should be found that will allow the prediction of the relative contribution of individual profiles. This could include specific chemical species, an understanding of how fuel or burn characteristics relate to the relative contribution of the two profiles, or a relationship between some measure of fire temperature and the VOC profiles. Second, the SOA and ozone formation potential of the two profiles should be determined. With this further work, the VOC profiles could be widely useful to model VOC emissions from many types of biomass burning in the western US, with additions to the framework being needed for fires that burn a lot of duff."

The present VOC emission profiles are able to describe the emissions from rotten wood burns; however, an appropriate VOC tracer should be found. For duff burns, the content of nitrogen-containing compounds is higher than for the other fuel components (e.g., canopy and litter), and the VOC composition may depend on the local environment. So, the VOC emissions from duff burns cannot be accurately predicted using the high-and low-temperature VOC profiles. In order to describe that duff burns are limitation of this methodology, a phrase has been added in Conclusions (line 725):

"With this further work, the VOC profiles could be widely useful to model VOC emissions from many types of biomass burning in the western US, with additions to the framework being needed for fires that burn a lot of duff."

MINOR/TECHNICAL COMMENTS

The language and presentation is some parts of the MS can be improved with more careful reading. Two examples are mentioned below: Abstract: Line 26: Precursors to the formation. . .. " the formation of.." is redundant.. Line 27: Measurements collected. . .. Measurements performed?

According to these comments, the corresponding points were fixed.

1	High- and low-temperature pyrolysis profiles describe volatile
2	organic compound emissions from western US wildfire fuels
3	
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24	
25	
26	Abstract. Biomass burning is a large source of volatile organic compounds (VOCs) and many
27	other trace species to the atmosphere, which can act as precursors to secondary pollutants such as
28	ozone and fine particles. Measurements <u>performed</u> with a proton-transfer-reaction time-of-flight
29	mass spectrometer during the FIREX 2016 laboratory intensive were analyzed with Positive
30	Matrix Factorization (PMF), in order to understand the instantaneous variability in VOC

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emissions from biomass burning, and to simplify the description of these types of emissions. 33 34 Despite the complexity and variability of emissions, we found that a solution including just two 35 emission profiles, which are mass spectral representations of the relative abundances of emitted 36 VOCs, explained on average 85% of the VOC emissions across various fuels representative of the western US (including various coniferous and chaparral fuels). In addition, the profiles were 37 38 remarkably similar across almost all of the fuel types tested. For example, the correlation 39 coefficient r^2 of each profile between Ponderosa pine (coniferous tree) and Manzanita (chaparral) is higher than 0.84. The compositional differences between the two VOC profiles appear to be 40 related to differences in pyrolysis processes of fuel biopolymers at high and low temperatures. 41 These pyrolysis processes are thought to be the main source of VOC emissions. "High-42 temperature" and "low-temperature" pyrolysis processes do not correspond exactly to the 43 commonly used "flaming" and "smoldering" categories as described by modified combustion 44 efficiency (MCE). The average atmospheric properties (e.g. OH reactivity, volatility, etc) of the 45 high- and low-temperature profiles are significantly different. We also found that the two VOC 46 47 profiles can describe previously reported VOC data for laboratory and field burns.

48 49

50 1 Introduction

51 Biomass burning is a large source of volatile organic compounds (VOCs) and other trace species to the atmosphere. Reactions involving these VOCs produce ozone and fine particles, 52 53 which are important air pollutants and radiative forcing agents (Alvarado et al., 2009; Alvarado 54 et al., 2015; Yokelson et al., 2009; Jaffe et al., 2012). Some VOCs from fires also have direct health effects (Naeher et al., 2007; Roberts et al. 2011). Biomass burning occurs in wildfires, 55 controlled burns of wildland and agricultural fuels, and in residential wood stoves and industrial 56 57 processes. Given the variety of fuels and burning conditions, it is unsurprising that the VOC composition of biomass burning emissions varies greatly between different fire states, locations, 58 and studies. Therefore, it is important to understand VOC emissions from biomass burning in 59 detail and develop a predictive capability that explains some of the variability in VOC emissions. 60 61 Multiple complex processes take place in biomass burning, including (i) distillation with release of water vapor and terpenes, (ii) pyrolysis of solid biomass giving off flammable gases, 62 (iii) flaming combustion, and (iv) non-flaming processes loosely lumped with smoldering 63

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Kanako Sekimoto 2018/4/26 16:21 削除: 9

Abby Koss 2018/4/23 13:30

削除: We identified the two VOC profiles as resulting from "high-temperature" and "lowtemperature" pyrolysis processes of fuel biopolymers, which are thought to be the main sources of the VOCs emissions from known to form VOCs in biomass burning.

Abby Koss 2018/5/3 19:

削除: This indicates that the high- and lowtemperature pyrolysis profiles could be widely useful to model VOC emissions from many types of biomass burning in the western US, with a few exceptions such as burns of duff and rotten wood. 77 combustion such as glowing (gasification) of biomass (Yokelson et al., 1996; Yokelson et al.,

78

79 of the polymers that form biomass such as cellulose, hemicellulose, and lignin. The temperature

1997; Collard and Blin, 2014; Liu et al., 2016). The main source of VOC emissions is pyrolysis

- 80 of the reaction and the physical characteristics of the biopolymer control which pyrolysis
- 81 mechanism (e.g. depolymerization, fragmentation, or aromatization) is the main source of
- 82 emitted VOCs (Yokelson et al., 1996; Yokelson et al., 1997; Collard and Blin, 2014; Liu et al.,
- 83 <u>2016</u>). In a given fire, the processes (i)-(iv) occur simultaneously, but the relative importance of
 84 each process <u>and temperature</u> can change with time, which relates to the variability in integrated
- VOC emissions between different fires. This variability is often parameterized as a function of modified combustion efficiency (MCE = $\Delta CO_2/(\Delta CO + \Delta CO_2)$) (Yokelson et al., 1996). CO₂ and CO are representative gases emitted from the flaming and smoldering combustion processes, respectively, and are measured in most biomass burning studies. MCE is generally higher in flaming combustion (> 0.9) and lower in smoldering combustion (< 0.9) (Akagi et al., 2011).
- The National Oceanic and Atmospheric Administration (NOAA) led the Fire Influence on 90 Regional and Global Environments Experiment (FIREX) 2016 laboratory intensive conducted at 91 92 the U.S. Forest Service Fire Sciences Laboratory in Missoula, Montana to study emissions of trace gases and aerosol from wildfires. Emissions from various fuels representative of the 93 western U.S. were sampled under controlled conditions by extensive instrumentation 94 95 (https://www.esrl.noaa.gov/csd/projects/firea/firelab/instruments.html). Experiments included 96 so-called stack burns, in which emissions from an evolving burn were entrained into a large-97 diameter stack and sampled by various instruments. VOCs were measured by several instruments, 98 including a PTR-ToF-MS (proton-transfer-reaction time-of-flight mass spectrometer) which captured gas-phase emissions with a fast time response during stack burns. The measurements 99 show variability in VOC composition as the fire shifts between a dynamic mix of distillation, 100 pyrolysis, flaming combustion, and "smoldering" combustion (here we use smoldering as a 101 102 rough term to include various "non-flame" processes such as gasification). Ions measured with the PTR-ToF-MS were interpreted using a combination of gas-chromatographic pre-separation 103 experiments, literature review, time-series analysis, and comparison to other instruments (Koss et 104 105 al., 2018). Approximately 90% of the instrument signal could be attributed to identified VOCs. 106 The aims of this work are to understand the variation in gas-phase emissions both over the

107 | course of a fire and on a fire-integrated basis. Ultimately, this improved understanding of

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emissions variability could be used to simplify predictions of the emission of secondary organic 117 aerosol (SOA) and ozone precursors. To do this, the VOCs observed by PTR-ToF-MS in stack 118 119 burns were analyzed using positive matrix factorization (PMF). We show that much of the 120 observed variability in VOCs can be explained by only two factors, and that these two factors are qualitatively related to the temperature of the pyrolysis processes, which are the main sources of 121 122 the VOC emissions from biomass burning. Based on this result, the two factors are named as a 123 high-temperature pyrolysis factor and a low-temperature pyrolysis factor. The two factors are compared between fuels. Importantly, the high-temperature factor is quantitatively similar 124 125 between different fuels, and the same is true for the low-temperature factor. The VOCs present in each factor are discussed in terms of composition, reactivity with OH, and propensity to form 126 127 secondary organic aerosol. The relative importance of high- and low-temperature pyrolysis 128 factors is quantified for each fuel and discussed with respect to physical properties of the fuel 129 and the burn dynamics. We also investigate how well VOC emissions in biomass burning can be modeled by the two PMF emission profiles through comparisons with previously reported data 130 131 from laboratory burns and wildfires. Finally, emissions of some specific compounds are 132 discussed.

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134

135 **2 Methods**

136 2.1 VOC measurements by PTR-ToF-MS

Fire emissions were measured during the FIREX 2016 intensive at the Fire Sciences
Laboratory in Missoula, Montana. The facility consists of a large combustion chamber and has
been described in detail previously (Christian et al., 2003; Christian et al., 2004; Burling et al.,
2010).

141 VOC measurements were performed using several instruments, including a PTR-ToF-MS. 142 This instrument employed a high-resolution ToF mass analyzer (Aerodyne Research Inc, MA, 143 USA; Tofwerk AG, Thun, Switzerland) and measured with a time resolution of 2 Hz. VOCs and 144 some inorganic compounds were ionized by proton transfer from H_3O^+ reagent ions. We include 145 the inorganic compounds in the discussion of VOCs. Species with a proton affinity higher than 146 that of water can be measured, which includes many unsaturated and polar compounds. The mass 147 resolution of the instrument (3000-5000 FWHM m/ Δ m) was sufficient to determine the

- elemental composition of ions and separate many isobaric compounds. Before each fire,
 background air in the combustion chamber was measured directly for several minutes. The
 instrument has been described in detail by Yuan et al. (2016; 2017), and operation, calibration,
 and peak identification during the FIREX 2016 laboratory intensive were described by Koss et al.
 (2018).
- 157

158 **2.2 Fuel and biomass burn descriptions**

159 Fifteen types of natural fuel mixtures, most of which are representative of important western 160 U.S. ecosystems, were burned (Table 1). The names below are largely taken from the dominant plant species: (i) Ponderosa pine, (ii) Lodgepole pine, (iii) Loblolly pine, (iv) Douglas fir, (v) 161 Engelmann spruce, (vi) Subalpine fir, (vii) Juniper, (viii) Bear grass, (ix) Ceanothus, (x) 162 163 Chamise-contaminated, (xi) Chamise-uncontaminated, (xii) Manzanita-contaminated, (xiii) Manzanita-uncontaminated, (xiv) Sagebrush, and (xv) Excelsior (aspen wood shavings). 164 "Contaminated" chaparral fuels (Manzanita and Chamise) were collected from a heavily air-165 polluted site near San Dimas, CA, while "uncontaminated" fuels were collected from a cleaner 166 167 site in North Mountain, CA. Individual components of various fuel complexes, including canopy, litter, duff, and rotten wood, were also burned separately. Fuel moisture content ranged from 168 169 0.6% to 55.6%, and instantaneous MCE ranged from 0.75 to 1. Additional details on the fires 170 and fuels are given by Selimovic et al. (2018) including: pre- and post-fire weight, weight of fuel 171 components, and elemental composition (C, H, N, S, and Cl by weight). Each fuel type was 172 burned several times. All fires consumed most of the fuel. The present experiments did not have 173 a direct measurement of temperature within the fire, which is not homogeneous and therefore 174 difficult to define. Rather, the air temperature of the emissions was measured by the FTIR instrument, located at the sampling inlet of the PTR-ToF-MS. The hot gases from the fire were 175 176 mixed with air from the room, cooling the air significantly, but the trends in temperature are 177 related to the initial temperature of the emitted gases.

178

179 **2.3 PMF analysis**

180 Data from 51 burns measured by PTR-ToF-MS (Table 1) were analyzed using positive
 181 matrix factorization (PMF), a numerical method that can be used to determine major
 182 compositional categories of emissions, their compositional profiles, and their relative

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enhancements over time. PMF was conducted using the PMF Evaluation Tool v. 2.08A (Ulbrich
et al., 2009). The basic principles of PMF and application to atmospheric chemistry
measurements have been previously described (Ulbrich et al., 2009; Paatero and Tapper, 1994;
Paatero, 1997).

More than 1000 ions were quantified in the PTR-ToF-MS mass spectra between m/z 12-217. 191 192 Of these, 574 were selected for PMF analysis (Table S1). These 574 ions were resolved from 193 neighboring peaks, were enhanced during at least one fire, and exclude primary (e.g., H_3O^+ and 194 $H_3O^+(H_2O)$) and contaminant ions (e.g., Teflon fragments and transition metals) (Koss et al., 195 2018). The ion signals (in units of normalized counts-per-second; ncps), which are normalized to the H_3O^+ ion intensities and corrected for ToF-duty cycle, humidity dependence, and H_3O^+ ion 196 depletion as described by Koss et al. (2018), were analyzed using PMF. Typically, raw ion 197 198 signals in units of "counts-per-second (cps)" have been used for PMF analysis. However, cps 199 VOC ion signals are affected by temporal variability (depletion and instability) in primary ion 200 intensity and humidity during the fire. To obtain PMF results that exclude instrument effects, the 201 normalized and corrected ion signals are used in this analysis. The uncertainties of the 202 normalized and corrected ion signals were calculated based on those originating from the raw 203 (cps) ion signals. We chose to use instrument signal rather than mixing ratio because many ion 204 masses cannot be unambiguously related to a single VOC contributor: they have several 205 contributors, or result from fragmentation, and cannot be converted to mixing ratio. For example, 206 $C_7H_{13}^+$ (*m/z* 97.101) is a fragmentary product ion of at least five different VOCs, whose relative 207 contributions are different between fires. However, variability in these ion signals still contains 208 information useful for PMF. To interpret the PMF results, we did convert to mixing ratio where 209 possible (Section 2.4). 528 compounds were quantified, of which 156 are identified VOCs. The PTR-ToF-MS measures 50-80% of total emitted non-methane VOC mass, with uncertainty in 210 211 this value due to semivolatile compounds (Hatch et al., 2017). 212 In this work, we applied PMF to extended time series, in which all fires of a particular fuel

type (e.g., Ponderosa pine) were consolidated into a single data matrix (Figure S1), as well as time series of single fire data. Each fuel type was burned several times. Some individual fires of a particular fuel did not necessarily capture the full possible range of high- and low-temperature fire conditions, because of variability in the relative amounts of fuel parts, fuel moisture content,

217 when fuel was added, or other differences. PMF using the consolidated time series makes it

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Kanako Sekimoto 2018/5/9 19:50 削除: 2017 221 possible to capture the widest possible range of fire conditions. This approach also simplifies the

comparison of average emission profiles between different types of fuels. Details on preparation
 of ion signal and uncertainty datasets are described in the Supporting Information (S1).

The discussion in Section 3 is based on the 2-factor PMF solutions. Out of the 574 ions, 434 ions were fitted well and together represented 99% of the total ion signal. A total of 140 ions were not well fitted as the difference between their measurements and the PMF reconstruction was higher than 50%; these ions are excluded from the factors presented here. Ulbrich et al. (2009) suggest that poor retrieval of ions with less than 5% of total signal is not uncommon.

229

230 2.4 Calculations of OH reactivity and volatility

231 To characterize key chemical properties of the emission profiles derived from PMF analysis, 232 we compare the OH reactivity and volatility of VOCs in each profile. These calculations require 233 conversion of the emission profiles from instrument signal (ncps) to mixing ratio (ppbv). 234 Fragment ions, cluster ions, and ions not well fitted by PMF were excluded from the 574 ions 235 used in PMF analysis and calibration factors were applied to the remaining 400 ions to convert 236 them to mixing ratio. Of these, 156 have known VOC contributors, and account for 90% of the 237 total instrument signal of non-primary and non-contaminant ions between m/z 12-217. (This 238 corresponds to an average of 92% of the total VOC concentration detected by PTR-ToF-MS). 239 Details on identification of the VOC contributors to ion masses and calibration are described by 240 Koss et al. (2018).

241 We quantified the importance of the 156 identified ions to OH chemistry by multiplying the 242 VOC + OH reaction rate coefficient (cm^3 /molecule/sec) with the VOC fraction in the profile (ppby VOC/ppby of total VOC emitted) with a scaling factor to convert from VOC molar 243 emission (ppby VOC) to number density (molecule/cm³ at experimental conditions of 900 mbar 244 and 26°C). The resulting OH reactivity is in units of per second per ppbv of total VOCs 245 246 measured with PTR-ToF-MS (1/sec/ppbv of total VOC emitted). For ions with more than one 247 contributor, a weighted average rate constant was determined. Rate constants were taken from the literature (Atkinson and Arey, 2003; NIST Chemical Kinetics Database; Cicerone and 248 249 Zellner, 1983; Gilman et al., 2015) or estimated from structurally similar VOCs. Details can be 250 found elsewhere (Koss et al., 2018).

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We also quantified volatility using the saturation concentration at 25 °C (C_0 , μ g m⁻³). 253 254 Saturation concentrations were taken from the literature (Rumble, 2017-2018; NIST Chemistry 255 WebBook; Yaws, 2015) where possible, and otherwise estimated based on the elemental 256 composition of the ion (Li et al., 2016). Volatility determined from elemental composition is 257 uncertain, especially for compounds with very low volatility where the uncertainty can be several 258 orders of magnitude (Li et al., 2016). We determined volatility for the 400 non-fragmentary ions. 259 We define volatility bins as follows, after Li et al. (2016): volatile organic compounds (VOC, C_0 $> 3 \times 10^6 \ \mu g \ m^{-3}$), intermediate volatility compounds (IVOC, $300 < C_0 < 3 \times 10^6 \ \mu g \ m^{-3}$), and 260 semivolatile compounds (SVOC, $0.3 < C_0 < 300 \ \mu g \ m^{-3}$). Separation into such volatility bins is 261 262 commonly used as an aid to discussion of SOA formation potential and gas/particle partitioning 263 (Donahue et al., 2011).

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265

266 3 Results and discussion

267 3.1 Two-factor parameterization of VOC emissions from biomass burning

268 Figure 1a shows the time series of selected VOC ion signals from burning a representative 269 mixture of Ponderosa pine fuels. In these lab fires, total VOC emissions (red line in Figure 1a) 270 often increase immediately and substantially during the initial combustion (for 170 seconds after 271 starting the burn in this example), and then total emissions gradually decrease as the flames die 272 out. Emissions of individual VOCs can be seen to fall into two categories: (i) higher emissions 273 during the first part of the fire, e.g. naphthalene, which correlates with the PMF factor we will largely attribute below to high-temperature pyrolysis (blue line in Figure 1a), and (ii) higher 274 275 emissions during the latter part of the fire, e.g., syringol, which correlates with the PMF factor 276 we will attribute below to low-temperature pyrolysis (green line in Figure 1a). This separation 277 into two categories is typical for most fires, with a few exceptions discussed later (e.g., burns of 278 duff and rotten wood).

These two PMF factors (Figure 1b) describe the total VOC emissions remarkably well for most fuels: residuals (the differences between the measured ion signals and the calculated ion signals based on the PMF fits) are less than 15% on average, except for Douglas fir, Engelmann spruce, and Subalpine fir for which the residual average is 20-25%. The residuals for individual fuels are summarized in Table 1c. For most of the fuels, the time series of the first and second 284 factors are strongly correlated with those of naphthalene and syringol, respectively (correlation

coefficient $(r^2) > 0.74$). On the contrary, emissions of compounds mainly from flaming or non-285 286 pyrolysis smoldering processes, such as CO, CO_2 , and NO_x (Figure 1c), do not correlate well 287 with the individual PMF factors (more detailed discussion is given in Section 3.5). This indicates that the two PMF factors do not correspond to the flaming and smoldering combustion processes 288 that are described by MCE and often referenced in biomass burning literature. The main source 289 290 of VOC emissions is pyrolysis of fuel biopolymers, and not the flaming and/or other combustion 291 processes. Therefore, we primarily attribute these two factors to high-temperature pyrolysis and 292 low-temperature pyrolysis, respectively, and will use these names to describe these factors in this 293 work. Our association between the factors and pyrolysis temperature is related more rigorously 294 to the distribution of products observed as a function of pyrolysis temperature in the next section. 295 When allowing more than two factors in PMF, the time series and mass spectral profiles of the 296 additional factors can be represented as an "intermediate" or "splitting" of high- and/or lowtemperature factors which can be described by a linear combination of the two factors. As 297 298 examples, Figures S2 and S3 show the correlation between *n*-factor solutions (n = 3, 4) and PMF 299 results from high- and low-temperature factors for Ponderosa pine datasets. This suggests that 300 only two factors, i.e., high- and low-temperature pyrolysis factors, were needed to explain most 301 of the variability we observed for the VOC emissions from biomass burning.

302 There are notable exceptions to the two-factor solution, including an infrequently observed, 303 but important, third factor that we call a "distillation" factor, and a fourth profile observed during 304 burns of duff. Several fires contain a distillation phase, in which a brief burst of VOCs, typically 305 enriched in terpenes, is emitted immediately prior to ignition. However, PMF captured this phase for only a limited number of burns in which the distillation phase contained sufficient gas-phase 306 307 emissions and lasted long enough (~30 seconds). When a two-factor solution is used, the 308 terpenes are largely grouped with the high-temperature pyrolysis factor. Duff is defined as a 309 "layer of moderately to highly decomposed leaves, needles, fine twigs, and other organic 310 material found between the mineral soil surface and litter layer of forest soil?" (Reardon, 2007). 311 The duff PMF solutions have residuals larger than 80% when solved with only two factors. This 312 means that duff burns have a unique VOC emission pattern that cannot be explained by only 313 high- and low-temperature factors. These exceptions are discussed in more detail later. 314

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321	3.2 VOC er	mission profiles	s of high- and	low-temperature	pyrolysis factors

322 The mass spectral profiles of the relative abundances of emitted VOCs for the individual 323 PMF factors obtained from a given fuel type are similar for replicate burns of the same fuel type. 324 When comparing the PMF profiles for two individual burns of the Ponderosa pine realistic mixture, the correlation coefficient (r^2) is higher than 0.92 for both the high- and low-325 326 temperature pyrolysis factors (Figure 2a). Importantly, the mass spectra for the high-temperature 327 pyrolysis factor are also very similar between different fuels, and the same is true for the low-328 temperature pyrolysis factor. For example, the correlations of each profile between (i) Douglas 329 fir and Ponderosa pine, (ii) Manzanita (chaparral) and Ponderosa, and (iii) Bear grass and Ponderosa have a slope near 1 and $r^2 \ge 0.83$ (Figures 2b-d). In contrast, the correlation between 330 the high- and low-temperature mass spectra is visually clearly lower ($r^2 < 0.69$ Figure 2e). Figure 331 332 3 shows the average VOC emission profiles of the two factors obtained using PMF results of 15 333 different fuels. The fractions of individual ion peaks in the emission profiles are summarized in Table <u>S1</u>. These average profiles are in good agreement with profiles of individual fuels: a best 334 fit of 0.96 < slope < 1.04 and r^2 > 0.84, except for high-temperature factor of Excelsior with r^2 = 335 336 0.68 (Table 1d and Figure S4). Excelsior is an unusual fuel in that it consists of fine shavings of 337 a single fuel component (wood). VOC composition in high- and low-temperature profiles is 338 discussed in Section 3.3.1. 339 The compositional differences between the two profiles can be qualitatively explained by the temperature of the pyrolysis reactions thought to be the main production mechanism of the 340 341 VOCs, such as depolymerization, fragmentation, and aromatization (Yokelson et al., 1996; 342 Yokelson et al., 1997; Collard and Blin, 2014; Liu et al., 2016). This is illustrated by the relative contributions from the high-temperature versus low-temperature factors for most emitted VOCs. 343 VOCs expected from high-temperature processes have a higher emissions contribution from the 344 345 high-temperature factor, and likewise for low-temperature VOCs and the low-temperature factor. 346 Figure 4a shows the contribution of each factor to selected pyrolysis products from major 347 fuel biopolymers, i.e., hemicellulose, cellulose, and lignin. The contributions of individual VOCs are expressed by their normalized fractions (F_{high-T} and F_{low-T}) of high- and low-temperature 348 factors: $F_{\text{high-T}} = Fraction_{\text{high-T}}/(Fraction_{\text{high-T}} + Fraction_{\text{low-T}})$ and $F_{\text{low-T}} = Fraction_{\text{low-T}}$ 349 350 $T/(Fraction_{high-T} + Fraction_{low-T}))$, where $Fraction_{high-T}$ and $Fraction_{low-T}$ correspond to fractions (in ppbv/total VOC ppbv) of individual species in the high- and low-temperature VOC profiles 351

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上へ移動 [1]: the temperature of the pyrolysis reactions thought to be the main production mechanism of the VOCs, such as depolymerization, fragmentation, and aromatization (Yokelson et al., 1996; Yokelson et al., 1997; Collard and Blin, 2014; Liu et al., 2016).

366 (Figure 3), respectively. Figure 4b also shows the relationship between pyrolysis temperature and 367 representative products for individual biopolymers as reported in the literature (Collard and Blin, 368 2014). During the heating of biomass, different chemical bonds within the biopolymers are 369 broken, which results in the release of VOCs and in rearrangement reactions within the matrix of 370 the residue. Low temperature pyrolysis breaks the bonds between the monomer units of the 371 polymers. Depolymerization in lignin (300-500 °C) produces guaiacols, (iso)eugenol, and 372 syringol. Furans and furfurals are dominantly formed from cellulose and hemicellulose (300-373 400 °C). Emissions of these compounds have a larger contribution from the low-temperature 374 factor ($F_{low-T} = 60-100\%$). Higher temperatures allow reaction of functional groups and covalent bonds in polymers and monomers. The resulting fragmentation emits various VOCs: for example, 375 376 hydroxyacetone, acetaldehyde, and acetic acid from depolymerization of cellulose and/or 377 hemicellulose. These VOCs have roughly equal contributions from low- and high-temperature 378 factors. The release of oxygenated compounds during depolymerization and fragmentation 379 increases the carbon percentage of the residual biopolymers. Benzene rings and aromatic 380 polycyclic structures form, which is termed char. Higher temperature pyrolysis breaks 381 progressively stronger bonds in char (> 500 °C). This aromatization process gives off aromatic 382 compounds with short substituents (e.g., phenol), non-substituted aromatics (e.g., benzene), and polycyclic aromatic hydrocarbons (PAHs such as naphthalene). Most of those aromatics have a 383 384 large contribution from the high-temperature factor ($F_{high-T} = 60-100\%$). As the temperature 385 increases, substituents of the aromatic rings disappear and PAHs are dominantly produced. This 386 is consistent with the contribution of the high-temperature factor to phenol ($F_{high-T} = 60\%$), 387 benzene (77%), and naphthalene (92%).

388 These many diverse chemical processes are likely happening simultaneously during a fire, and their relative intensities may change based on fuel composition, fuel moisture content, or 389 390 other as-vet poorly defined parameters. However, the net result of all these variables is the 391 emission of just two major compositional groups. The VOCs that comprise these two groups 392 mostly consist of the pyrolysis products described above and their analogs. During most of these 393 fires, the emissions of any particular VOC can be described by a linear combination of the high-394 temperature and low-temperature pyrolysis time series. Some VOCs are emitted mainly from the 395 high-temperature pyrolysis; some mainly from the low-temperature profile; and others have a 396 mixed contribution. This is quantified by F_{high-T} as described above. We sorted the VOCs by

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401 F_{high-T_2} to show how the chemical composition of emissions changes from high- to low-402 temperature pyrolysis process. Figure 5 shows the chemical characteristics of compounds that 403 are mostly emitted in the high-temperature pyrolysis ($F_{high-T} = 80-100\%$ in panel (a)), mostly 404 emitted in the low-temperature pyrolysis ($F_{high-T} = 0.20\%$ in panel (e)), or have mixed contributions from both pyrolysis ($F_{high-T} = 60-80\%$ in panel (b), 40-60% in (c), and 20-40% in 405 406 (d)). F_{high-T} of each individual VOC is shown in Figure S5. In the category emitted mostly by the 407 high-temperature pyrolysis, important compounds include alkyl-substituted aromatics and aliphatic alkenes (Figures 5a and b), whereas carbonyls have more equal contributions from the 408 409 high- and low-temperature pyrolysis processes. It should be noted that terpenes (e.g., (oxygenated) monoterpenes and isoprene) emitted from distillation are grouped with the high-410 temperature pyrolysis (Figures 5a and b; Section 3.6). 411 412 Several nitrogen (N)-containing compounds also fall into high or low temperature categories

consistent with behavior previously reported in the literature. The main N-containing compounds 413 detected by PTR-ToF-MS are isocyanic acid (HNCO), nitrous acid (HONO), hydrogen cyanide 414 415 (HCN), and ammonia (NH₃). HNCO, HONO, and HCN have a high contribution of the high-416 temperature factor (F_{high-T} = 80-100% in Figure 5a), while NH₃ falls into the category with a large contribution from the low-temperature factor ($F_{low-T} = 86\%$ in Figure 5e). Nitrogen in 417 biomass typically exists as amino acids/proteins and pyrrole/pyridine (aromatic N-heterocycles). 418 419 During the pyrolysis of those N-functionalities at high temperature (700-1100 °C), HCN is 420 identified as the main product in most cases (Johnson and Kang, 1971; Haidar et al., 1981; 421 Patterson et al., 1968; Houser et al., 1980). NH₃, resulting from the lower-temperature pyrolysis 422 of proteins, has been classified as smoldering combustion gases and falls here into the low 423 temperature profile (Yokelson et al., 1996).

The present analysis predominantly focuses on VOCs. The VOC emissions from biomass burning are dominated by pyrolysis reactions of biopolymers. However, not all species are emitted from pyrolysis reactions. For example, flaming combustion releases CO_2 , NO_x , HONO, and black carbon, etc. This is a separate process and cannot be expected to be captured by our VOC framework. In Section 3.5 we show that MCE, which delineates flaming versus smoldering combustion, is a poorer descriptor of VOC variability than the high versus low-temperature pyrolysis framework.

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435 3.3 Chemical characteristics of VOC emissions depending on pyrolysis temperature

436 3.3.1 VOC composition

437 The VOC emission profiles for the high- and low-temperature factors are shown in Figure 3 438 and they mainly consist of hydrocarbons, oxygenates with n=1-7 oxygen atoms, and nitrogenand/or sulfur-containing hydrocarbons (Figure 6). In each emission profile, about half of the 439 440 fraction (in ppbv) is accounted for by a combination of the following seven compounds: (i) 441 ethene (C_2H_4) , (ii) formaldehyde (HCHO), (iii) methanol (CH₃OH), (iv) acetaldehyde (CH₃CHO), (v) acrolein (CH₂=CHCHO), (vi) acetic acid (CH₃COOH) and glycolaldehyde 442 443 (HOCH₂CHO), and (vii) ammonia (NH₃). The other half includes several fundamental structures, with a variety of functionalities, as discussed later. Oxygenates with one oxygen are predominant 444 in both emission profiles, accounting for 39% of molar emissions in the high-temperature profile 445 446 and 36% in the low-temperature profile. Emissions of highly oxygenated compounds (≥ 2 oxygen atoms) and ammonia are higher in the low-temperature profile than in the high-447 448 temperature profile. The fractions of hydrocarbons and compounds that contain both N and O, 449 such as HNCO, are lower in the low-temperature profile.

VOCs emitted from biomass burning can be generally organized into major structural groups: furans, aromatics, oxygenated aromatics, aliphatic compounds, and so on. Within each structural category, compounds can have various functionalities, such as alcohol or alkene substituents (Hatch et al., 2015). VOC composition classified by 11 structures and 17 functionalities is shown in Figures 7 and 8. Some VOCs have multiple functional groups. These are counted once in each relevant category. For example, guaiacol is counted in "Oxygenated aromatic" structural category as "Alcohol" and "Ether (methoxy)" functional groups.

457 The most dominant emissions are attributable to aliphatic oxygenates, i.e., 62% of molar emissions in the high-temperature profile and 60% in the low-temperature profile (Figure 7). 458 459 This is due to the specific compounds (ii)-(vi) described above. The low-temperature profile is twice as rich in aromatic oxygenates (≥ 2 oxygen atoms) and furans as the high-temperature 460 461 profile, while the high-temperature profile is enriched in aliphatic (mostly alkenes) and aromatic hydrocarbons. Terpenes (including isoprene, monoterpenes, sesquiterpenes, and oxygenated 462 463 monoterpenes) emitted from distillation, not from pyrolysis, are dominantly grouped with the high-temperature factor. Compared to the low-temperature profile, the high-temperature profile 464 is enriched in the following functional groups: C-C double bond (>C=C<), C-C triple bond (-465

- 466 C \equiv C-), diene (>C=C-C=C<), polycyclic aromatic hydrocarbon (PAH), nitrile (-C \equiv N), amide (-
- 467 C(=O)-N-), nitro (-NO₂), nitrate (-NO₃), thiol/sulfide (-S-(H)) (Figure 8). The low-temperature
- 468 profile is enriched in alcohols (-OH), ethers (mostly methoxy groups: -O-CH₃), esters (-C(=O)-
- 469 O-), and amines (-NH₂; mostly ammonia). The emissions of compounds with carbonyl groups
- 470 (>C=O) and acids (-C(=O)-OH-) are similar. These results are consistent with the contributions
- 471 of VOC to the high- and low-temperature factors described in Section 3.2.
- 472

473 **3.3.2 OH reactivity**

The hydroxyl radical (OH) is an important driver of daytime oxidation chemistry. 474 475 Ouantifying the VOC reactivity with OH provides insight into which VOC emissions may be 476 most important for ozone and secondary organic aerosol (SOA) formation. Interestingly, the two 477 profiles have a similar average per-molecule (weighted by abundance) rate constant with OH: 15.7×10^{-12} cm³/molecule/s for the high-temperature profile and 15.8×10^{-12} cm³/molecule/s for 478 the low-temperature profile. However, the reactivity is provided by very different VOCs in each 479 480 profile. Aliphatic oxygenates are important in both profiles, but more so in the high-temperature profile (30% of reactivity) than in the low-temperature profile (24% of reactivity). In the high-481 482 temperature profile, the reactivity also has a large contribution from terpenes and aliphatic 483 hydrocarbons, while in the low-temperature profile, the reactivity is largely due to furans and 484 aromatics (Figure 9a). Since the total VOC emissions in real-world fires come from a mixture of 485 the high- and low- temperature pyrolysis factors, the total OH reactivity of fresh emissions 486 should scale directly with VOC concentration.

487

488 3.3.3 Volatility

Volatility is another important chemical characteristic affecting secondary organic aerosol 489 490 (SOA) yield and formation rate. The low-temperature emission profile contains more compounds that are of higher molecular weight, more oxygenated, and of lower volatility (Figure 9b). 491 Oxygenated aromatics have been shown to be important biomass burning SOA precursors (Bruns 492 et al., 2016), and while the SOA yields of many other compounds are unknown, the lower 493 494 volatility and higher oxygen content of the low-temperature profile suggests a potentially more 495 efficient SOA formation. SOA formation was also studied during the FIREX 2016 campaign, by oxidizing emissions in a chamber, and will be presented separately (Lim et al, in prep, 2018). We 496

Abby Koss 2018/4/25 20:30 削除: can be estimated from the relative importance of the high- and low-temperature pyrolysis in a given fire

- note that the compounds with $C_0 < 10^2 \ \mu g \ m^{-3}$ shown in Figure 9b should be primarily in the 500 particle phase and not measureable by PTR-MS without long delay times (Pagonis et al., 2017). 501 502 However, the volatility of these compounds (calculated from the elemental composition) has an 503 uncertainty of several orders of magnitude. Also, the cyclic compounds that are abundant in the 504 low-temperature profile, such as aromatic oxygenates, produce multifunctional ring-opening-505 products that are known to be efficient SOA precursors (Yee et al., 2013). In a similar manner to 506 the OH reactivity, the total volatility distribution can be estimated from the relative importance 507 of the high- and low-temperature pyrolysis in a given fire.
- 508

3.4 Relationship of fuel characteristics to relative importance of high- and low-temperature pyrolysis factors

511 To use the PMF profiles (Figure 3) for estimates of VOC emissions from other fires, it is 512 necessary to know the relative fire-integrated contributions of high- and low-temperature pyrolysis for those fires. As a step in this direction, in the present work, we found that fire-513 514 integrated molar emission ratios of total VOCs from high-temperature pyrolysis to low-515 temperature pyrolysis, $\sum VOC_{high-T}$ (in ppbv)/ $\sum VOC_{low-T}$ (in ppbv), are related to which parts of 516 the plants are burned (blue bars in Figure 10). When leafy fuels (i.e., canopy, shrub, and 517 herbaceous fuels) are burned, the fraction of total VOC emissions originating from high-518 temperature pyrolysis is higher than those from low-temperature pyrolysis. These results imply 519 that surface-to-volume ratios and the content of biopolymers in a given fuel can strongly affect 520 the relative importance of high- and low-temperature pyrolysis. Leaves have high surface-to-521 volume ratios and despite higher fuel moisture, at least the surface may tend to heat up easily, 522 resulting in a higher contribution from the high-temperature factor. The higher monoterpene 523 content of foliage may explain why low-temperature distillation products like monoterpenes are 524 associated with the high-T pyrolysis factor.

In contrast, the burn of rotten wood was found to contain VOC emissions from lowtemperature pyrolysis only. Our brown rotten wood samples were enriched in lignin (Kirk and Cowling, 1984). Lignin is relatively resistant to thermal decomposition compared to cellulose and hemicellulose. The temperature range where pyrolytic decomposition occurs significantly is 280-500 °C for lignin, 240-350 °C for cellulose, and 200-260 °C for hemicellulose (Liu et al., 2016; Babu, 2008), as shown in Figure 4b. In our laboratory fires, the rotten wood first

531 smoldered for an extended period, and then flames were observed. However, only the low-532 temperature profile was observed. This suggests that it is more difficult for lignin-rich fuels to 533 reach high enough temperatures to emit the "high-temperature pyrolysis" VOCs. Therefore, we 534 do not see the same gradient in pyrolysis products that is observed for other fuel burns mainly consisting of cellulose and hemicellulose. Nitrogen content and speciation also vary between 535 536 different biomass components, and temperature and differences in biopolymer content have been 537 shown to strongly affect the composition of nitrogen-containing emissions (Hansson et al., 2004; Ren et al., 2011; Coggon et al. 2016). This is consistent with the observed differences in nitrogen 538 539 speciation between the two profiles.

540

541 3.5 High- and low-temperature pyrolysis profiles describe total VOC emissions

542 Previous studies have found a correlation between the emission factors of certain VOCs and 543 the fire-integrated modified combustion efficiency (MCE) (Yokelson et al., 1996: Yokelson et al., 1997; Selimovic et al., 2018). Thus, one might expect that the high- and low-temperature 544 545 pyrolysis factors would also show a strong relationship to MCE. However, MCE does not 546 parameterize the relative amounts of high- and low-temperature pyrolysis products very well. either instantaneously or on a fire-integrated basis (Figure 11). The basic reason is that CO₂ as 547 well as NO_x are emitted overwhelmingly from flaming combustion, which is *not* the main source 548 549 of most VOC emissions, and these emissions are not expected to correlate with a linear 550 combination of the high- and low-temperature pyrolysis processes, while CO emissions are 551 reasonably well correlated with an average of high- and low-temperature emissions (Figures 1 552 and S6). This is especially clear in rotten log burns, where CO_2 and the PMF profiles are not correlated. The CO₂ emissions are enhanced by shifting from the smoldering to flaming 553 554 combustion, but VOC emission patterns are not changed from the low- to high-temperature pyrolysis (Figure S7). Consequently, CO_2 and MCE, which indicate the separation between 555 556 flaming and smoldering combustions, are not appropriate to estimate the high-/low-temperature pyrolysis VOC emissions. Our results indicate that VOC emissions are even more closely 557 correlated to the biopolymer composition and the surface-to-volume ratios of fuels, than to the 558 559 MCE. It is also seen that for some fires the air temperature correlates with the high-temperature contribution (e.g., Fires #37 and #59 shown in Figure S8a-c). This suggests that the VOC 560 emissions are certainly related to the temperature within a fire. However, some other burns did 561

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565	not have a good correlation between the temperature and VOC emissions (e.g., Fire #38 shown
566	in Figure S8d), because the temperature measurement had some issues in the present work: (i)
567	background temperature for each burn was different, (ii) some burns have colder temperature at
568	end compared to start, which means that the laboratory was not controlled at constant
569	temperature, and (iii) the increase in air temperature often lagged behind the emissions,
570	especially at the start of a fire.

571 <u>The relative contributions from the high- and low-temperature processes could be estimated</u>
 572 from ratios of distinct marker species that are consistently enhanced in the high and low 573 temperature profiles. Several such pairs were considered and the ratio of ethyne (C₂H₂) to furan
 574 (C₄H₄O) can reasonably predict the ratio of high- to low-temperature emissions as given in Eq. 1:

 $\frac{\text{total VOC ,high temperature (ppbv)}}{\text{total VOC ,high temperature (ppbv)}} = \frac{\text{ethyne (ppbv) / 0.0393}}{\text{total VOC ,high temperature (ppbv)}}$

575

576 577

total VOC, low temperature (ppbv) furan (ppbv) / 0.0159

(1)

The derivation and how the ethyne/furan ratio correlates with the high-/low-temperature
emission ratio are given in the Supporting Information (S2 and Figure S9). However, this pair is
not ideal because measurements of these two species are not frequently available and furan has
high reactivity to both O₃ and NO₃ radicals. Future work should assess non-PTR measurements
in order to find appropriate external markers.

Studies of laboratory burns and wildfires have reported variable emission ratios (or factors) 583 for various VOCs as well as fire-integrated MCE, even for similar fuel types. Here we 584 investigate how well total VOC emissions in biomass burning can be fit by the average VOC 585 emission profiles (Figure 3) using emission factors and ratios reported in the literature for 586 587 laboratory and field burns (Gilman et al., 2015; Stockwell et al., 2015; Akagi et al., 2011). When 588 fitting the present high- and low-temperature factors to the other biomass burning data, total 589 VOC emissions can be described with different relative fractions of the factors (Figure S10). For 590 example, the best fit to a laboratory study by Gilman et al. (2015), using fuels from southwestern, 591 southeastern, and northern U.S. (e.g., pine, spruce, fir, chaparral, mesquite, and oak) with MCE = 0.75-0.98, includes 32% high-temperature and 68% low-temperature VOC emissions; for 592 593 another laboratory study by Stockwell et al. (2015) including several types of grass, spruce, and chaparral with MCE = 0.68-0.99, 59% high temperature and 41% low temperature; temperate 594 forest fires (MCE = 0.95) reported by Akagi et al. (2011), 77% high temperature and 23% low 595

temperature, while in the case of chaparral fires (MCE = 0.96), 48% high temperature and 52% 596 597 low temperature. The fitting can be done with high correlation coefficient ($r \ge 0.92$) for all the 598 literature data (Figure S10). This is further evidence that at most two factors can explain the 599 majority of VOC variability. Therefore, these two factors could be used to fill in VOCs not measured in the other studies which sometimes had less chemical detail. The current study 600 601 incorporated a wide range of MCEs and fuel moisture contents (Table 1), so the two-factor 602 description may be applicable under many conditions. However, some other factors should be required for specific burns, as discussed below. 603

604

605 **3.6 Emission of specific compounds**

606 **3.6.1 Distillation phase**

607 At the beginning of many burn experiments, a white smoke is visible immediately prior to ignition. This "distillation phase" does not result from pyrolysis or combustion, but rather a 608 609 gradual heating and release of water and volatile compounds trapped within the biomass. This phase of the fire was not distinguished by PMF. The distillation phase from coniferous fuels is 610 611 enriched in some compounds highly relevant to atmospheric chemistry, especially terpenes (Koss et al., 2018). But this phase lasts only a short time (typically less than 10 seconds), in which only 612 613 a short spike in emissions is observed. Accordingly, PMF cannot capture this phase effectively 614 even if a large number of factors is chosen. As an exception, the distillation phase of Sagebrush, 615 enriched in terpenes and a specific oxygenated monoterpene (camphor), can be distinguished as a 616 third PMF factor, because that phase lasted longer than 30 seconds in that fire. The reported 617 overall residual of 15% includes the poorly fitted distillation phase, and we stress that it typically 618 accounts for only a small portion of the overall emissions. Additionally, with the exception of terpenes, the composition of the distillation profile is similar to that of the high-temperature 619 profile. 620

For some fuel burns other than coniferous fuels (e.g., Manzanita), VOC emissions during the distillation phase are quite small, although distillation smoke is visible. In these cases, PMF incorporates this phase into the low-temperature pyrolysis factor. There may be a relationship between the VOC emission process coincident with distillation (low- or high-temperature) and the presence of visible smoke. For instance, perhaps here the temperatures are low enough that the compounds are able to re-condense into visible smoke.

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629 **3.6.2 Duff burn**

A fourth factor can be resolved from the PMF analysis of duff burns. The distribution of VOC structures and functionality in the duff emission profiles (Figure <u>12a</u>) is similar to the lowtemperature pyrolysis profile (Figure <u>12b</u>). The major difference is much higher emission of aliphatic nitrogen-containing compounds: 56% more of these compounds are emitted per-ppbv VOC in the duff profile than in the low-temperature profile. The additional emissions are mostly nitriles and amides, especially hydrogen cyanide (HCN), acetonitrile, and acetamide. Pyrroles and pyridines are also enhanced, but are much less abundant overall.

The organic portion of duff is enriched in nitrogen relative to other components of coniferous fuels. The nitrogen to carbon ratio in the Subalpine fir duff (N:C ratio = 0.028 by weight) was a factor of 2.1 higher than the average of other Subalpine fir components, and the Engelmann spruce duff N:C ratio (0.022) was 1.3 times higher than other Engelmann spruce components. Coggon et al. (2016), who investigated VOC emissions from the burning of herbaceous and arboraceous fuels, also found that the nitrogen-containing fraction of VOCs emitted from biomass burning increased with the nitrogen content of the fuel.

However, the nitrogen content cannot entirely explain why duff has a unique emission profile. 644 645 Other fuels, such as Ceanothus and Ponderosa pine litter, have similar N:C ratios (0.025, 0.024, 646 and 0.022, respectively) but are explained well by the 2-factor PMF solution consisting of high-647 and low-temperature pyrolysis factors. The contradiction may be due to differences in the 648 speciation of nitrogen-containing organics. In woody and leafy fuels, proteins and amino acids 649 account for 80-85% of the organic nitrogen (Ren and Zhao, 2015). In soils, proteins account for 650 typically only 40% of organic nitrogen, and heterocyclic nitrogen compounds (pyrroles and 651 pyridines) account for 35% (Schulten and Schnitzer, 1997). Pyrolysis of nitrogen heterocycles releases HCN, while proteins and amino acids may release more NH₃ (Leppälahti and Koljonen, 652 653 1995). This is consistent with the higher HCN and nitriles characteristic of the duff emission 654 profile.

19

655

656 3.6.3 Variation in specific VOCs between fuels

- 657When comparing emission profiles of individual fuels to the average profiles shown in658Figure 3, there are some specific compounds whose emissions are notably higher (> ×5) or lower
- $(< \times 0.2)$ than the average (Figure S4). Here we highlight several key features:
- (i) For Ponderosa/Lodgepole/Loblolly pines, Douglas/Subalpine firs, and Juniper, the
 emission of benzoquinone (C₆H₄O₂·H⁺, m/z 109.028) is quite low in the hightemperature pyrolysis: 7-21% of the average emission for the pines and firs, and 2%
 for Juniper (Figures S4a-1~4, 6, and 7).
- 664 (ii) For fuels other than coniferous fuels and Sagebrush, i.e., Bear grass, Excelsior, 665 Ceanothus, Chamise, and Manzanita, emissions of monoterpenes ($C_{10}H_{16}$ ·H⁺, *m/z* 137.132) are only 2-15% of the average (Figures S4a-8~14).
- 667(iii) Excelsior emits especially low quantities of nitrogen-containing compounds,668especially nitriles (hydrogen cyanide, acetonitrile, acrylonitrile, and propane nitrile)669and pyridine, in the high-temperature pyrolysis (Figure S4a-9). This is because the670nitrogen content in Excelsior is significantly lower than other fuels. The Excelsior671N:C ratio (0.005 by weight) is 3.6 times lower than the average of other fuels (0.017672 \pm 0.006).
- (iv) High-temperature pyrolysis of Ceanothus produces quite high emission of
 benzofuran-type compounds (Figure S4a-10). Benzofuran (C₈H₆O·H⁺, *m/z* 119.049)
 and methylbenzofuran and possibly its isomer such as cinnamaldehyde (C₉H₈O·H⁺, *m/z* 133.065) are 5.5 and 10.1 times higher than the average, respectively.
- 677 (v) Sage<u>brush</u> specifically emits camphor ($C_{10}H_{16}O \cdot H^+$, *m/z* 153.127) in high-678 temperature pyrolysis (Figure S4a-15).
- (vi) There are a limited number of exceptions in low-temperature profiles (Figure S4b).
 This means that low-temperature pyrolysis gives almost identical VOC emissions,
 independent of fuel types.
- 682

683 4 Conclusions

This work focused on interpretation of VOC emissions from biomass burning. We provided an understanding of VOC variability based on known chemical and physical processes to release VOCs from fires. We explained most of the observed variability between VOC emissions from fuel types and over the course of a fire using just two emission profiles: (i) high-temperature

- 688 pyrolysis profile and (ii) low-temperature pyrolysis profile. The results are summarized as689 follows:
- 690 1. The two profiles can explain the variability in VOC emissions composition between
 691 different fuel types and over the course of individual fires, with an average residual of <
 692 15%.
- 693 2. The high-temperature profile is quantitatively similar between different fuel types ($r^2 > 0.84$), and likewise for the low-temperature profile.
- 3. The two profiles are significantly different in terms of VOC composition, volatility, and
 contributors to OH reactivity. The high-temperature pyrolysis profile is enriched in
 aliphatic unsaturated hydrocarbons, (polycyclic) aromatic hydrocarbons, terpenes
 (emitted from distillation), HCN, HNCO, and HONO. The resulting OH reactivity is
 primarily attributed to terpenes, aliphatic hydrocarbons, and non-aromatic oxygenates.
 The low-temperature pyrolysis profile is enriched in aromatic oxygenates, furans, and
 NH₃. The OH reactivity is contributed significantly by furans and aromatics.
- 4. The fire-integrated molar emission ratios of total VOCs from high-temperature pyrolysis to low-temperature pyrolysis are related to the biopolymer composition and surface-to-volume ratios of fuels. Higher surface-to-volume ratios lead to total VOC emissions enriched in products resulting from high-temperature pyrolysis than from those resulting from low-temperature pyrolysis.
- 7075. The two VOC profiles can model previously reported VOC data for laboratory and field708burns ($r \ge 0.92$). This suggests that these two profiles could be used to fill in VOCs not709actually measured in the previous studies which sometimes had less chemical detail.
- 6. MCE, which parameterizes flaming and smoldering combustion, is not appropriate to
 estimate the high-/low-temperature pyrolysis VOC emissions. This suggests that the
 high- and low-temperature pyrolysis profiles may provide information on emissions that
 is not accessible with a broader definition of smoldering combustion implicit in the use
 of MCE.
- 715 7. Duff burns emit a specific VOC profile which is similar to that of low-temperature
 716 pyrolysis, but additionally includes aliphatic nitrogen-containing compounds, especially
 717 HCN, acetonitrile, and acetamide.

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Our framework provides a way to understand VOC emissions variability in other laboratory and 719 720 field studies of biomass burning. We highlight two areas of useful future work. First, external 721 tracers should be found that will allow the prediction of the relative contribution of individual 722 profiles. This could include specific chemical species, an understanding of how fuel or burn 723 characteristics relate to the relative contribution of the two profiles, or a relationship between 724 some measure of fire temperature and the VOC profiles. Second, the SOA and ozone formation 725 potential of the two profiles should be determined. With this further work, the VOC profiles could be widely useful to model VOC emissions from many types of biomass burning in the 726 727 western US, with additions to the framework being needed for fires that burn a lot of duff.

Future work should <u>also</u> include a quantitative comparison of the VOC PMF results to measurements of aerosol, inorganic gases, and organic species not measured by PTR-ToF-MS. Such a comparison would help define the relationship between VOCs and characteristics of primary organic aerosol (POA). We note that the primary aerosols have also been shown to have distinct profiles that correlate with different pyrolysis and combustion processes in the fire (Reece et al., 2017; Haslett et al., 2017).

734 735

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understand VOC emission variability in other laboratory and field studies of biomass burning.

753 References

- Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J.
 D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmos. Chem. Phys., 11, 4039-4072, https://doi.org/10.5194/acp-11-4039-2011, 2011.
- Alvarado, M. J., Wang, C, and Prinn, R. G.: Formation of ozone and growth of aerosols in young
 smoke plumes from biomass burning: 2. Three-dimensional Eulerian studies, J. Geophys. Res.,
 114 (D9), D09307, http://doi.org/10.1029/2008JD011186, 2009.
- Alvarado, M. J., Lonsdale, C. R., Yokelson, R. J., Akagi, S. K., Coe, H., Craven, J. S., Fischer, E.
 V., McMeeking, G. R., Seinfeld, J. H., Soni, T., Taylor, J. W., Weise, D. R., and Wold, C. E.:
 Investigating the links between ozone and organic aerosol chemistry in a biomass burning
- plume from a prescribed fire in California chaparral, Atmos. Chem. Phys., 15 (12), 6667-6688,
 http://doi.org/10.5194/acp-15-6667-2015, 2015.
- Atkinson, R. and Arey, J. Atmospheric degradation of volatile organic compounds, Chem. Rev.,
 103 (12), 4605-4638, <u>http://doi.org/10.1021/cr0206420</u>, 2003.
- Babu, B. V.: Biomass pyrolysis: a state-of-the-art review. Biofuels, Bioprod. Bioref., 2, 393-414,
 http://dpo.org/10.1002/bbb.92, 2008.
- Bruns, E. A., El Haddad, I., Slowik, J. G., Kilic, D., Klein, F., Baltensperger, U. and Prévôt, A. S.
 H.: Identification of significant precursor gases of secondary organic aerosols from residential
 wood combustion., Sci. Rep., 6, 27881, doi:10.1038/srep27881, 2016.
- Burling, I. R., Yokelson, R. J., Griffith, D. W. T., Johnson, T. J., Veres, P., Roberts, J. M.,
 Warneke, C., Urbanski, S. P., Reardon, J., Weise, D. R., Hao, W. M., and de Gouw, J.:
 Laboratory measurements of trace gas emissions from biomass burning of fuel types from the
 southeastern and southwestern United States, Atmos. Chem. Phys., 10, 11115-11130,
 https://doi.org/10.5194/acp-10-11115-2010, 2010.
- 778 Christian, T. J., Kleiss, B., Yokelson, R. J., Holzinger, R., Crutzen, P. J., Hao, W. M., Saharjo, B.
- H., and Ward, D. E.: Comprehensive laboratory measurements of biomass-burning emissions:
- 780 1. Emissions from Indonesian, African and other fuels, J. Geophys. Res., 108 (D23), 4719,
- 781 <u>http://doi.org/10.1029/2003JD003704</u>, 2003.

- 782 Christian, T. J., Kleiss, B., Yokelson, R. J., Holzinger, R., Crutzen, P. J., Hao, W. M., Shirai, T.,
- and Blake, D. R.: Comprehensive laboratory measurements of biomass-burning emissions: 2.
- First intercomparison of open-path FTIR, and GC-MS/FID/ECD, J. Geophys. Res., 109 (D2),
- 785 D02311, <u>http://doi.org/10.1029/2003JD003874</u>, 2004.
- Cicerone, R. J., and Zellner, R.: The atmospheric chemistry of hydrogen cyanide (HCN), J.
 Geophys. Res., 88 (C15), 10689-10696, <u>http://doi.org/10.1029/JC088iC15p10689</u>, 1983.
- 788 Coggon, M. M., Veres, P. R., Yuan, B., Koss, A., Warneke, C., Gilman, J. B., Lerner, B. M.,
- 789 Peischl, J., Aikin, K. C., Stockwell, C. E., Hatch, L. E., Ryerson, T. B., Roberts, J. M.,
- 790 Yokelson, R. J., and de Gouw, J. A.: 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(18), 9903–9912,
 doi:10.1002/2016GL070562, 2016.
- Collard, F. X., and Blin, J.: A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin, Renew. Sustainable Energy Rev., 38, 594-608, http://doi.org/10.1016/j.rser.2014.06.013, 2014.
- Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility
 basis set: 1. Organic-aerosol mixing thermodynamics, Atmos. Chem., Phys., 11, 3303-3318,
 http://doi.org/10.5194/acp-11-3303-2011, 2011.
- Gilman, J. B., Lerner, B. M., Kuster, W. C., Goldan, P. D., Warneke, C., Veres, P. R., Roberts, J.
 M., de Gouw J. A., Burling, I. R., and Yokelson, R. J.: Biomass burning emissions and
 potential air quality impacts of volatile organic compounds and other trace gases from fuels
 common in the US, *Atmos. Chem. Phys.*, 15 (24), 13915-13938, <u>http://doi.org/10.5194/acp-</u>
 15-13915-2015, 2015.
- Haidar, N. F., Patterson, J. M., Moors, M., and Smith, W. T.: Effects of structure on pyrolysis 806 807 Food. Chem., 29 gases from amino acids, J. Agric. (1),163-165, http://doi.org/10.1021/jf00103a040, 1981. 808
- 809 Hansson, K.-M., Samuelsson, J., Tullin, C. and Åmand, L.-E.: Formation of HNCO, HCN, and
- 810 NH3 from the pyrolysis of bark and nitrogen-containing model compounds, Combust. Flame,
- 811 137 (3), 265–277, doi:10.1016/J.COMBUSTFLAME.2004.01.005, 2004.

- 812 Haslett, S. L., Thomas, J. C., Morgan, W. T., Hadden, R., Liu, D., Allan, J. D., Williams, P. I.,
- 813 Sekou, K., Liousse, C., and Coe, H.: Highly-controlled, reproducible measurements of aerosol
 814 emissions from African biomass combustion, Atmos. Chem. Phys. Discuss.,
 815 http://doi.org/10.5194/acp-2017-679, in review, 2017.
- 816 Hatch, L. E., Luo, W., Pankow, J. F., Yokelson, R. J., Stockwell, C. E., and Barsanti, K. C.:
- 817 Identification and quantification of gaseous organic compounds emitted from biomass
- 818 burning using two-dimensional gas chromatography–time-of-flight mass spectrometry, Atmos.
- 819 Chem. Phys., 15, 1865-1899, https://doi.org/10.5194/acp-15-1865-2015, 2015.
- Hatch, L. E., Yokelson, R. J., Stockwell, C. E., Veres, P. R., Simpson, I. J., Blake, D. R.,
 Orlando, J. J., and 724 Barsanti, K. C.: Multi-instrument comparison and compilation of non methane organic gas emissions from biomass burning and implications for smoke-derived
 secondary organic aerosol precursors, Atmos. Chem. Phys., 17, 1471-1489, 10.5194/acp-17 1471-2017, 2017.
- Houser, T. J., McCarville, and M. E., Biftu, T.: Kinetics of the thermal decomposition of
 pyridine in a flow system, Int. J. Chem. Kinet., 12 (8), 555-568,
 <u>http://doi.org/10.1002/kin.550120806</u>, 1980.
- Jaffe, D. A., and Wigder, N. L.: Ozone production from wildfires: A critical review, Atmos.
 Environ., 51, 1-10, http://doi.org/10.1016/j.atmosenv.2011.11.063, 2012.
- Johnson, W. R., and Kan, J. C.: Mechanisms of hydrogen cyanide formation from the pyrolysis
 of amino acids and related compounds, J. Org. Chem., 36 (1), 189-192, http://doi.org/10.1021/jo00800a038, 1971.
- Kirk, T. K., and Cowling, E. B.: Biological decomposition of solid wood, Adv. Chem., 207 (12),
 455-487, http://doi.org/10.1021/ba-1984-0207.ch012, 1984.
- Koss, A. R., Sekimoto, K., Gilman, J. B., Selimovic, V., Coggon, M. M., Zarzana, K. J., Yuan,
 B., Lerner, B. M., Brown, S. S., Jimenez, J. L., Krechmer, J., Roberts, J. M., Warneke, C.,
- 837 Yokelson, R. J., and de Gouw, J.: Non-methane organic gas emissions from biomass burning:
- identification, quantification, and emission factors from PTR-ToF during the FIREX 2016
- laboratory experiment, Atmos. Chem. Phys., <u>18, 3299-3319</u>, https://doi.org/10.5194/acp-<u>18-</u>
 3299-2018, 2018.

- Leppälahti, J., and Koljonen, T.: Nitrogen evolution from coal, peat and wood during
 gasification: Literature review, Fuel Process. Technol., 43, 1-45, <u>http://doi.org/10.1016/0378-</u>
 3820(94)00123-B, 1995.
- Li, Y., Pöschl, U., and Shiraiwa, M.: Molecular corridors and parameterizations of volatility in
 the chemical evolution of organic aerosols, Atmos. Chem. Phys., 16 (5), 3327-3344,
 http://doi.org/10.5194/acp-16-3327-2016, 2016.
- Lim, C., Hagan, D., Cappa, C., Coggon, M., Koss, A., Sekimoto, K., de Gouw, J., Warneke, C.,
 Kroll, J. Laboratory studies on the aging of biomass burning emissions: chemical evolution
 and secondary organic aerosol yield, in preparation, 2018.
- Liu, W. -J., Li, W. -W., Jiang, H., and Yu, H. -Q.: Fates of chemical elements in biomass during
 its pyrolysis, Chem. Rev., 117 (9), 6367-6398, <u>http://doi.org/10.1021/acs.chemrev.6b00647</u>,
 2016.
- Mackie, J. C., Colket, M. B., III, and Nelson, P. F.: Shock tube pyrolysis of pyridine, J. Phys.
 Chem., 94 (10), 4099-4106, <u>http://doi.org/10.1021/j100373a040</u>, 1990.
- 855 Manion, J. A., Huie, R. E., Levin, R. D., Burgess D. R., Jr., Orkin, V. L., Tsang, W., McGivern,
- W. S., Hudgens, J. W., Knyazev, V. D., Atkinson, D. B., Chai, E., Tereza, A. M., Lin, C. -Y.,
 Allison, T. C., Mallard, W. G., Westley, F., Herron, J. T., Hampson, R. F., and Frizzell, D. H.:
- 858 NIST Chemical Kinetics Database, NIST Standard Reference Database 17, Version 7.0 (Web
- Version), Release 1.6.8, Data version 2015.12, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899-8320. Web address: http://kinetics.nist.gov/,
- last access: 28 November 2017, 2017.
- 862 Naeher, L. P., Brauer, M., Lipsett, M., Zelikoff, J. T., Simpson, C. D., Koenig, J. Q., and Smith,
- K. R.: Woodsmoke health effects: A review, Inhal. Toxicol., 19 (1), 67-106,
 https://doi.org/10.1080/08958370600985875, 2007.
- 865 NIST Chemistry WebBook, Web address: <u>http://webbook.nist.gov/chemistry/</u>, last access: 28
 866 November 2017, 2017.
- Paatero, P., and Tapper, U.: Positive matrix factorization: A non-negative factor model with
 optimal utilization of error estimates of data values, *Environmetrics*, 5 (2), 111-126,
 http://doi.org/10.1002/env.3170050203, 1994.
- 870 Paatero, P.: Least squares formulation of robust non-negative factor analysis, Chemometr. Intell.
- 871 Lab., 37 (1), 23-35, <u>https://doi.org/10.1016/S0169-7439(96)00044-5</u>, 1997.

- 872 Pagonis, D., Krechmer, J. E., de Gouw, J. A., Jimenez, J. L. and Ziemann, P. J.: Effects of gas-
- 873 wall partitioning in Teflon tubing and instrumentation on time-resolved measurements of gas-
- phase organic compounds, Atmos. Meas. Tech., 10, 4687–4696, doi:10.5194/amt-2017-279,
 2017.
- Patterson, J. M., Tsamasfyros, A., and Smith, W. T.: Pyrolysis of pyrrole, J. Heterocycle Chem.,
 5 (5), 727-729, <u>http://doi.org/10.1002/jhet.5570050527</u>, 1968.
- 878 Reardon, J.: Duff. *In:* FireWords: Fire Science Glossary [electronic]. U.S. Department of
 879 Agriculture, Forest Service, Rocky Mountina Research Station, Fire Science Laboratory
 880 (Producer). Available: http://www.firewords.net, last update 2007.
- Reece, S. M., Sinha, A., and Grieshop, A. P.: Primary and photochemically aged aerosol
 emissions from biomass cookstoves: Chemical and physical characterization, Environ. Sci.
 Technol., 51 (16), 9379-9390, http://doi.org/10.1021/acs.est.7b01881, 2017.
- 884 Ren, Q., Zhao, C., Chen, X., Duan, L., Li, Y. and Ma, C.: NO_x and N₂O precursors (NH₃ and
- HCN) from biomass pyrolysis: Co-pyrolysis of amino acids and cellulose, hemicellulose and
 lignin, Proc. Combust. Inst., 33(2), 1715–1722, http://doi.org/10.1016/J.PROCI.2010.06.033,
- 887 2011.
- Ren, Q., and Zhao, C.: Evolution of fuel-N in gas phase during biomass pyrolysis, Renew. Sust.
 Energ. Rev., 50, 408-418, http://doi.org/10.1016/j.rser.2015.05.043, 2015.
- Roberts, J. M, Veres, P. R., Cochran, A. K., Warneke, C., Burling, I. R., Yokelson, R. J., Lerner,
 B., Gilman, J. B., Kuster, W. C., Fall, R., and de Gouw, J.: Isocyanic acid in the atmosphere
- and its possible link to smoke-related health effects, Proc. Natl. Acad. Sci., 208 (22), 8966893 8971, http://doi.org/10.1073/pnas.1103352108, 2011.
- 894 Rumble, J. R. CRC Handbook of Chemistry and Physics, 98th Ed. (2017-2018).
- Schulten, H. –R. and Schnitzer, M.: The chemistry of soil organic nitrogen: a review, Biol. Fert.
 Soils., 26, 1-15, 1997.
- Selimovic, V., Yokelson, R. J., Warneke, C., Roberts, J. M., de Gouw, J., 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.*, <u>18</u>, <u>2929-</u>
 2948, http://doi.org/10.5194/acp-18-2929-2018, 2018.
- 901 Stockwell, C. E., Veres, P. R., Williams, J., and Yokelson, R. J.: Characterization of biomass
- 902 burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution

- proton-transfer-reaction time-of-flight mass spectrometry, Atmos. Chem. Phys., 15 (15), 845865, <u>http://doi.org/10.5194/acp-15-845-2015</u>, 2015.
- Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation
 of organic components from Positive Matrix Factorization of aerosol mass spectrometric data,
- 907 Amos. Chem. Phys., 9 (9), 2891-2918, <u>http://doi.org/10.5194/acp-9-2891-2009</u>, 2009.
- Yaws, C. L.: The Yaws Handbook of Vapor Pressure: Antoine Coefficients, Elsevier Science,2015.
- 910 Yee, L. D., Kautzman, K. E., Loza, C. L., Schilling, K. A., Coggon, M. M., Chhabra, P. S., Chan, 911 M. N., Chan, A. W. H., Hersey, S. P., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and 912 Seinfeld, J. H.: Secondary organic aerosol formation from biomass burning intermediates: 913 methoxyphenols, Chem. Phys., 13 8019-8043, phenol and Atmos. (16),
- 914
 http://doi.org/10.5194/acp-13-8019-2013, 2013.
- Yokelson, R. J., Griffith, D. W. T., and Ward, D. E.: Open-path Fourier transform infrared
 studies of large-scale laboratory biomass fires, J. Geophys. Res. Atmos., 101 (D15), 21067-
- 917 21080, <u>http://doi.org/10.1029/96JD01800</u>, 1996.
- Yokelson, R. J., Susott, R., Ward, D. E., Reardon, J., and Griffith, D. W. T.: Emissions from
 smoldering combustion of biomass measured by open-path Fourier transform infrared
 spectroscopy, J. Geophys. Res. Atmos., 102 (D15), 18865-18877,
 <u>http://doi.org/10.1029/97JD00852</u>, 1997.
- Yokelson, R. J., Crounse, J. D., de Carlo, P. F., Karl, T., Urbanski, S., Atlas, E., Campos, T.,
 Shinozuka, Y., Kapustin, V., Clarke, A. D., Weinheimer, A., Knapp, D. J., Montzka, D. D.,
- 924 Holloway, J., Weibring, P., Flocke, F., Zheng, W., Toohey, D., Wennberg, P. O., Wiedinmyer,
- 925 C., Mauldin, L., Fried, A., Richter, D., Walega, J., Jimenez, J. L., Adachi, K., Buseck, P. R.,
- 926 Hall, S. R., and Shetter, R.: Emissions from biomass burning in the Yucatan, Atmos. Chem.
- 927 Phys., 9 (15), 5785-5812, <u>http://doi.org/10.5194/acp-9-5785-2009</u>, 2009.
- 928 Yuan, B., Koss, A., Warneke, C., Gilman, J. B., Lerner, B. M., Stark, H., and de Gouw, J. A.: A
- high resolution time-of-flight chemical ionization mass spectrometer utilizing hydronium ions
- 930 $(H_3O^+ ToF-CIMS)$ for measurements of volatile organic compounds in the atmosphere,
- 931 Atmos. Meas. Tech., 9 (6), 2735-2752, <u>http://doi.org/10.5194/amt-9-2735-2016</u>, 2016.

- 932 Yuan, B., Koss, A., Warneke, C., Coggon, M., Sekimoto, K., and de Gouw, J. A.: Proton-
- transfer-reaction mass spectrometry: Applications in atmospheric sciences, Chem. Rev., 117
- 934 (21), 13187-13229, http://doi.org/10.1021/acs.chemrev.7b00325, 2017.

935 Table 1. (a) Data numbers and corresponding details of 15 different fuels used in PMF analysis. (b) Average MCE and fuel

936 moisture content. (c) Residuals of 2-factor PMF solutions. (d) Correlation with average VOC emission profile (Figure 3).

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Final Engl		(a) Data number for consolidated PMF			(b) Fire characteristics		(c) Residual [%] ^a	(d) Correlation with average VOC emission profile (Figure 3)				Unknown
Fuel								High-temperature pyrolysis factor		Low-temperature pyrolysis factor		まず本面。フィントレイ茶) Timese Navy
	Total	Detail			MCE	Moiture content	Average ± STDV (maximum, minimum)	Slope	Correlation coefficient (r ²)	Slope	Correlation coefficient (r ²)	青式変史: フォント:(央) TIMES NEW Poman 14 pt 大字
		Realistic	5	(Fire 01, 02, 37, 59, 72)	0.913-0.940	24.3-31.8%						Troman, 14 pr, X-
1 Ponderosa nine	10	Canopy	2	(Fire 19, 39)	0.904-0.935	40.4-51.1%	15.7 ± 7.6 (28.9, 7.7)	$\textbf{0.976} \pm \textbf{0.004}$	0.9393	1.012 ± 0.005	0.9245	
iii onderosa pine	10	Litter	1	(Fire 38)	0.945	6.2%						
		Rotten log	2	(Fire 13, 73)	0.932-0.957	2.9-5.7%						-
		Realistic	4	(Fire 06, 07, 58, 63)	0.927-0.943	20.3-24.4%						
2. Lodgepole pine	7	Canopy	1	(Fire 40)	0.924	49.30%	14.8 ± 4.9 (23.3, 10.9)	0.990 ± 0.004	0.9586	0.990 ± 0.002	0.9716	
		Litter	2	(Fire 21, 41)	0.925-0.938	7.0-10.5%						-
3. Loblolly pine	2	Litter	2	(Fire 35, 53)	0.922-0.929	5.4-10.9%	6.3 ± 0.3 (6.6, 6.1)	0.989 ± 0.007	0.8662	0.960 ± 0.004	0.8862	·.
		Realistic	2	(Fire 14, 57)	0.926-0.951	23.3-25.7%						
4. Douglas fir	4	Canopy	1	(Fire 18)	0.928	50.3%	21.2 ± 9.3 (34.9, 14.9)	0.996 ± 0.004	0.9508	0.999 ± 0.003	0.9563	
		Litter		(Fire 43)	0.951	3.0%						-
		Realistic	1	(Fire 08)	0.920	13.0%	20.5 ± 2.4 (22.2, 18.8) ^b	0.999 ± 0.006 b	0.9019 ^b	0.960 ± 0.004 ^b	0.9004 ^b	
5. Engelmann spruce	3	Canopy	1	(Fire 25)	0.950	34.0%						
		Dutt		(Fire 26)	0.817	0.6%	82.0				·····	-
		Realistic	2	(Fire 47, 67) (Fire 15, 22)	0.932-0.942	32.8-35.6%	22.0 + 14.1 (45.2, 0.1)	1 001 + 0 005	0.0250.0	0.000 + 0.002 0	0.0547.0	
6. Subalpine fir	6	Canopy	2	(Fire 15, 25) (Fire 51)	0.886-0.947	17.0-55.5%	$23.0 \pm 14.1 (43.2, 9.1)^{-1}$	1.001 ± 0.005	0.9559	0.999 ± 0.003	0.9547	
		Duff		(Fire 51)	0.906	0.0%	87.0					
7. Juniper	2	Canopy		(Fire 68, 75)	0.928-0.939	45 0-48 0%	6.4 ± 3.0 (8.5, 4.3)		0.8872			-
8. Bear grass	1			(Fire 62)	0.897	55.1%	5.6	1.039 ± 0.006	0.8847	1.006 ± 0.004	0.9174	<i>.</i>
9. Excelsior	2			(Fire 49, 61)	0.945-0.971	3.9-5.4%	6.2 ± 3.0 (8.3, 4.0)	1.04 ± 0.01	0.6806	1.012 ± 0.007	0.8521	-
10. Ceatnothus	2	Shrub	2	(Fire 69, 74)	0.942-0.947	17.7-27.9%	10.2 ± 1.1 (11.0, 9.5)	1.000 ± 0.007	0.8416	1.030 ± 0.006	0.8985	
11. Chamise (contaminated)	3	Canopy	3	(Fire 24, 29, 46)	0.948-0.959	10.9-16.1%	13.1 ± 3.9 (16.0, 8.6)	1.037 ± 0.006	0.8951	1.044 ± 0.004	0.9477	-
12. Chamise (uncontaminated)	3	Canopy	3	(Fire 27, 32, 48)	0.946-0.954	6.2-17.1%	12.6 ± 2.0 (14.2, 10.4)	$\textbf{1.017} \pm \textbf{0.005}$	0.9322	1.024 ± 0.004	0.9299	-
13. Manzanita (contaminated)	2	Canopy	2	(Fire 30, 33)	0.962-0.963	23.5-26.7%	13.0 ± 1.1 (13.8, 12.3)	$\textbf{0.997} \pm \textbf{0.004}$	0.9347	1.034 ± 0.004	0.9504	-
14. Manzanita (uncontaminated)	2	Canopy	2	(Fire 28, 34)	0.963-0.964	25.7-26.3%	7.3 ± 1.1 (8.0, 6.5)	1.015 ± 0.005	0.9229	1.043 ± 0.005	0.9224	_
15. Sagebrush	2	Shrub	2	(Fire 66, 71)	0.919-0.922	37.8-54.2%	7.0 ± 2.1 (8.5, 5.6)	0.993 ± 0.005	0.9046	1.011 ± 0.004	0.9306	

* Residual [%] = [Total measured ion signal - Total synthetic ion signal of high- and low-temperature factors] / Total measured ion signal x 100 b "Duff" data is excluded.



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940Figure 1. Results for an example burn of Ponderosa pine realistic mixture (Fire #37). (a)941Time series of ion signals of 574 ion peaks, naphthalene ($C_{10}H_8 \cdot H^+$, m/z 129.070), and942syringol ($C_8H_{10}O_3 \cdot H^+$, m/z 155.070). (b) PMF results of 2-factor solution. The grey and pink943colors are stacked, not overlapped. (c) Time series of mixing ratios of CO2, CO, and NOx944measured by open-path Fourier transform infrared (OP-FTIR) optical spectroscopy and945the modified combustion efficiency (MCE) (Selimovic et al., 2018). The MCE trace is946colored by the key and scale on the right.



(e) Low-temperature vs. High-temperature pyrolysis factor



Figure 2. Comparison of mass spectral profiles: (a) Ponderosa pine realistic mixture (Fire #72) vs. Ponderosa pine realistic mixture (Fire #02) for high- and low-temperature pyrolysis factors. (In this case, PMF was separately performed for data of Fire #02 and #72.) (b) Douglas fir vs. Ponderosa pine for high- and low-temperature factors. (c) Manzanita (contaminated) vs. Ponderosa pine for both the factors. (d) Bear grass vs. Ponderosa pine for both the factors. (e) Low- vs. high-temperature pyrolysis factor for Ponderosa pine and Manzanita (contaminated). Data points in individual panels correspond to well-fitted 434 ion peaks. Slope and correlation coefficient (r^2) are obtained using logarithmic fraction, i.e., log(ncps/total VOC ncps).

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Figure 3. Average VOC emission profiles of high- and low-temperature pyrolysis factors, obtained using consolidated PMF results of 15 different fuels.



Figure 4. (a) Normalized fraction of factors for selected biomass pyrolysis products, obtained using PMF results of 15 different fuels. (b) Diagram of the relationship between pyrolysis temperature and products for hemicellulose, cellulose, and lignin, as reported in the literature (Collard and Blin, 2014). Individual color bars show the temperature range to form specific products described by chemical structures.



Figure 5. Contributions, shown as normalized fractions, of VOCs relative to the high- and low-temperature factors: (a) $F_{\text{High-T}} = 100-80\%$ and $F_{\text{Low-T}} = 0-20\%$, (b) $F_{\text{High-T}} = 80-60\%$ and $F_{\text{Low-T}} = 20-40\%$, (c) $F_{\text{High-T}} = 60-40\%$ and $F_{\text{Low-T}} = 40-60\%$, (d) $F_{\text{High-T}} = 40-20\%$ and $F_{\text{Low-T}} = 60-80\%$, and (e) $F_{\text{High-T}} = 20-0\%$ and $F_{\text{Low-T}} = 80-100\%$. In this figure, molar emissions (in units of ppbv) of all the ion peaks in VOC emission profiles (Figure 2b) are described. The inner circle in each pie chart shows the elemental composition of the emissions. The outer circle provides more detailed information on specific compounds, structures, and functionalities found in each group. Details of molar fractions in each category are summarized in Table <u>\$2</u>.

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Figure 6. VOC composition in the high- and low-temperature emission profiles.



Figure 7. VOC composition in (a) high-temperature pyrolysis and (b) low-temperature pyrolysis emission profiles (Figure 3) sorted by 11 structural categories and 17 functional groups. Some VOCs have multiple structures. These are counted once in each relevant category. For example, benzofuran is counted in the structural categories of "Oxy. aromatic" and "Furans" as "Not substituted/alkyl" functional group. Structures detected with low abundance (<0.002 ppbv/total VOC ppbv) are mostly not-substituted or alkyl-substituted.



Figure 8. VOC composition in high- and low-temperature pyrolysis emission profiles (Figure 3) sorted by 17 functional groups. Each group includes various structures and elemental composition. Some VOCs have multiple functional groups. These are counted once in each relevant category. For example, guaiacol is counted in the categories of "Alcohol" and "Ether (methoxy)".





Figure 9. High- and low-temperature emission profiles compared by (a) OH reactivity and (b) volatility, described by saturation concentration (μ g m⁻³).





Figure 10. Ratios of fire-integrated molar emissions <u>of total VOCs from high- to low-</u> <u>temperature pyrolysis</u> ("∑VOC_{High-T}/∑VOC_{Low-T}") for different type fuel parts, obtained using PMF results of 15 different fuels.

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Figure 11. The comparison of contribution of high-temperature factor versus modified combustion efficiency (MCE). (a) Time series of Fire #37 (Ponderosa pine realistic mixture). (b) Scatter plot of instantaneous high-temperature contribution versus MCE for all Ponderosa pine fires. (c) Scatter plot of fire-integrated high-temperature contribution versus MCE for all fires. Contribution of high-temperature factor was calculated by $\Sigma VOC_{high-T}/(\Sigma VOC_{high-T} + \Sigma VOC_{how-T})$ instantaneously or on a fire-integrated basis.





Figure <u>12</u>. (a) VOC emission profile of duff burn of Engelmann spruce and Subalpine fir. (b) Scatter plot of duff emission profile (Engelmann spruce) versus average low-temperature pyrolysis profile.

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