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Atmospheric Chemistry and Physics Discussions

Interactive comment on "High- and low-temperature pyrolysis profiles describe volatile organic compound emissions from western US wildfire fuels" *by* Kanako Sekimoto et al.

Anonymous Referee #2

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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"

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.

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.

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.

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.

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?

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.

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?

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