

Review of acp-2019-1179

Review

February 18, 2020

1 General Comments

This paper uses a flow tube reactor to simulate the atmospheric oxidation potential of organic molecular markers emitted from burning peat and eucalyptus. The peat fires smoldered while the eucalyptus ones flamed. The semi-volatile organic markers were measured off-line using GC-MS or IC-PAD. The study was able to identify the reaction potential and the formation of semi-volatile organic markers that are common to chemical mass balance models and source apportionment studies.

The study topic is good for *ACP*. The results are timely because oxidation flow reactors (OFRs) are coming into vogue, and we need to better understand the results that OFRs produce and the potential air quality implications. With that, the study data have value and should be published. However, this particular study also has some serious limitations that need to be better addressed.

For one, the paper organization makes it seem like there are two separate studies, an emissions study and an OFR study. The emissions part of the paper is substantially less useful because all of the semi-volatile markers were observed in past studies and reported about repeatedly. Additionally, the discussion on emissions lacks information about how these peat burning results are different than other forms of vegetation burning and what that may or may not mean for emissions reactivity. More critical thinking is warranted to help emphasize how the peat burning emissions are going to impact the SOA compared with other biomass fuels. Otherwise, it does not belong at the forefront of the paper currently. The best approach may be to emphasize the emissions work less and get to the OFR results sooner.

The lack of replicate tests is another serious study limitation. It appears that standard deviations were taken from another set of tests and applied. This makes it difficult to judge the quality of the concentration data given here and calls into question how exactly the statistics were performed. It also complicates the interpretation of evidence showing what reacted or formed. This is a major limitation that needs to be addressed by providing the readers with sample population (N) and a detailed description of how the standard deviation was calculated and used to determine statistical significance and so on.

Finally, no new emissions compounds or SOA markers were measured that weren't part of the original compound suite. At the very least a set of chromatograms should be provided showing the raw emissions and the OFR effluent. That way we can see the major changes in these emissions.

More specific comments that may help remedy these major deficiencies are given below.

2 Specific comments

1. line 13: conserve use of the term 'significant' for describing statistics results.
2. line 48: Biomass burning particles exhibit a variety of toxicological properties other than mutagenicity. It is worth being clear about that.
3. lines 54-59: **[MAJOR]** Resolving the organic chemical composition of biomass burning particles is indeed challenging and improvements in speciation are needed. However, this particular study doesn't improve speciation technology in any way. It examines a common set of polar organic compounds and simulates their potential to photooxidize in the atmosphere. The suggestion is to focus on the reactivity of these molecules not on the improved speciation seeing that there are no methodological improvements in molecular level speciation being presented *per se*. After this study, we are still near 80% w/w for the unknown chemical fraction.
4. lines 61-72: This study uses peat as the main BB fuel. Be more specific about the importance of peat burning and why there needs to be a global emphasis on peat burning emissions.

5. lines 80:81: I think the paper needs to be written around this sentence. This is what will make this study novel, important, and worth reading to many. Try and get to this point sooner. It would be better to couch this paper as one that attempts to examine the stability of commonly used polar atmospheric organic markers in an oxidizing environment.
6. lines 81-93: Describe the advantages and disadvantages of each of these studies, how these pertain and give rise to the current study. Describe more than what these studies did, i.e, mention why these studies are important and are worthy of further discussion. Otherwise, there is not much value here.
7. lines 95-96: All peats except Eucalyptus? Why not just focus on peats?
8. lines 97-98: Describe why the focus here was isolated to polar compounds. It may have been more interesting to focus on the most reactive compounds in the aerosol mixture instead of presenting the study as an exercise in chemical accounting.
9. lines 135-140: At what depth were the tropical and Russian peats extracted?
10. lines 176-179: Briefly mention the mass of fuel used per test and how the fuels were configured for burning.
11. lines 203-207: Figure 1 does not indicate which on-line instruments were used. These instruments should be described. Please explain how they were used. If they aren't being used as part of this study please explain why. There is no modified combustion efficiency evidence showing the levels of smoldering or flaming combustion for each fuel type. Perhaps that can be included here.
12. lines 229-231 and lines 251-258: It is mentioned that a ^{13}C radio-labeled levoglucosan sample was added as internal standard. Wouldn't the ^{13}C isotope elute at the same time as the unlabeled compound? How was that accounted for in this study. The radio isotopes are typically applied for GC-MS. How did things work with the IC-PAD method knowing that the PAD is a non-specific detector and that the radio isotope may interfere?
13. lines 236-237: What is the value of reporting these separately considering that the equilibrium partitioning changes and was specific to the sampling conditions used for this particular study? Please discuss briefly. Also, was any thermodynamics-based check performed on how well the equilibrium partitioning was measured here? Such a relatively straightforward check on select compounds can verify that the sampling worked as planned.
14. lines 275-280: **[MAJOR]** Please clarify how the SDs were calculated. It's unclear where the standard deviations (SDs) came from and the reader should know exactly what and how many experiments were used to report SD values. The suggestion that the SDs came from another study and therefore can be applied here is questionable analytical-chemical practice. SDs should be experiment-specific, not just assumed and carried-over from study to study. At the very least, multiple injections of the same extract should be performed. What is meant by 'similar' fuels? This comment applies to all of the experimental data being reported.
15. lines 282-328: This information about methoxy-phenol emissions from biomass burning is already available *ad nauseum* in the literature and can be further consolidated. Instead of focusing on what we already know, examine how the peat emissions are different (if they indeed are) and how these differences may be important to the atmospheric processing and oxidation. Knowing more about the extent of smoldering and flaming combustion can help properly develop this discussion.
16. lines 381-508: **[MAJOR]** Again, virtually all of this chemical information is already available. Much of this can be condensed into a brief paragraph or two unless there is something salient and different for the fuels being examined here that merits further attention. **Suggestions:** Develop one section that discusses 'Polar organic chemistry' of these emissions. Move the figures of individual compound emissions into supporting information. Develop a new emission figure that combines everything by compound class and shows the reader some sort of chemical mass balance so they can understand the aerosol fraction of interest (more like Figure 3, but include a mass balance). Only if needed, focus on some of the unique chemical or physical state attributes of individual compounds emitted during burning of these particular fuels. In other words, if the chemical structure or physical state of a compound is important to understanding its oxidation then discuss these attributes and the results. This requires a reorganization of the paper as some of these results are presented elsewhere.

17. line 509: It would be interesting to learn if any of the levoglucosan was found in the gas phase. Levoglucosan elutes from a GC column with and without derivatization. Was there any indication of levoglucosan in the gas-phase?
18. lines 524-530: The important part of the study begins here. Figure 3 is a good figure that captures the essence of what was tested, measured, and and accomplished.
19. Figure 3: Again, are these error bars taken from other studies? If so, please remove them from the figure. One idea is to combine all of the peat samples measured here and calculate a standard deviation and use that to report global error for experimental peat burning. That can be added as a panel to one of the figures or presented separately.
20. lines 605-614: The importance of associating meaningful error with concentration data cannot be understated. For example, the error associated with levoglucosan measurement using GC-MS is approximately 20%. Although, the combustion test error can bring this value closer to 30%-50%. If we knew the exact error associated with repeating these peat experiments, we'd have a better understanding of this decrease being real or not. This may also explain why the same compound appears to be either formed or degraded for some fuels (see lines 631-632 and lines 691-699 (*e.g.*, hexanoic acid)).
21. line 696: Please describe the type of statistical tests being applied here and how they are being applied. Please report the sample population (N). Additionally, provide more information about how the error was calculated and applied to conduct the statistics tests.
22. lines 724-733: Please describe the criteria for a "top" contributing compound. Was it concentration?
23. lines 736-737: Isn't it also possible that the combustion was different?