

## Summary:

This work describes laboratory studies to comprehensively characterize gases and particles in fresh and aged peat biomass burning organic aerosol (BBOA). A Potential Aerosol Mass Oxidation Flow Reactor (PAM-OFR) was used to oxidize peat emissions. Filter-based measurements provided PM<sub>2.5</sub> mass concentrations, elemental concentrations, eight different thermally-resolved carbon fractions (OC, EC, pyrolyzed carbon), organic acids, water soluble organic carbon, carbohydrate concentrations, NH<sub>4</sub>, and HNO<sub>3</sub> concentrations. Mass reconstruction and moisture content analyses are also provided.

This manuscript addresses a lack of peat BBOA related source profiles, providing a wealth of information on gas- and particle-phase peat BBOA chemical composition with and without atmospheric aging. The intercomparison between peat samples from six locations to represent different biomes is particularly novel. Although this work has the potential to be highly useful for future source apportionment studies, I do not recommend publication unless major revisions are made. In particular, there is very little information provided on PAM-OFR operation characteristics, which makes it extremely difficult to assess whether the reactor was used properly to mimic atmospherically relevant conditions. In reading this paper, it seems as though there have been two additional manuscripts submitted using this data set and/or these techniques (Watson et al., 2019, and Cao et al., 2019), and although they are repeatedly cited, they have not yet been peer reviewed/published (per the citations), so I was unable to verify if the necessary information has been provided in these works. This significantly weakens the impact of this work, since the techniques are neither verifiable nor repeatable.

Specific suggestions for improvement are provided in the following general and technical/minor comments.

## General Comments:

1. BBOA oxidation is incredibly challenging to characterize using a PAM-OFR due to chemical and physical heterogeneity and rapid/complex kinetics. More attention should therefore be given to contextualizing the results presented here in light of PAM-OFR challenges. The PAM wiki is a useful site that provides recommendations for reactor operation ([https://sites.google.com/site/pamwiki/hardware/tutorial\\_and\\_recs](https://sites.google.com/site/pamwiki/hardware/tutorial_and_recs)).
  - a) In general, there is a lack of information provided regarding PAM-OFR operating conditions. What were the flow rates (and by extension residence times) through the PAM-OFR? What were dilution ratios? Were dilution ratios kept constant for samples collected before and after the PAM-OFR? Was the reactor allowed to reach steady state prior to sample collection? What were typical photon fluxes measured at each oxidation condition? Without this information, the results are entirely without context and essentially meaningless.
  - b) How was the OFR calibrated for these studies (e.g., with SO<sub>2</sub>? CO? With or without BBOA)? It seems that this is not the only manuscript to come out of this data set – is the PAM-OFR calibration procedure discussed in related articles? However, it would be good to provide even a basic description of calibration details here, perhaps in the supplement.
  - c) Was external OH reactivity ( $\text{OHR}_{\text{ext}} \sim \sum k_i c_i$ , where  $k_i$  is the OH reaction rate constant for species  $i$  and  $c_i$  is the concentration of reacting species  $i$ ) characterized in this or other studies? Peng et al. (2015, 2016) and Li et al. (2015) describe suppression of OH by interfering VOC species. The  $\text{OHR}_{\text{ext}}$  should be characterized/estimated for your system, particularly because many different VOCs generated from biomass burning can react externally with OH. It should be explicitly stated whether or not parallel gas-phase measurements (e.g., from a PTR-MS) were conducted. If so, the authors should provide some analysis and discussion about how the measured VOCs potentially interfered with their  $\text{OHR}_{\text{ext}}$ . If not, hopefully the authors attempted to remove VOCs (e.g., with VOC denuders), or, failing to at least do that, provide some discussion about the *potential* for

interference. Without any attention to this caveat of OFR experiments, the results are questionable.

- d) With OFR-185, photolysis at both 254 nm and 185 nm may occur, particularly at high light intensities. Peng et al. (2016) provides a detailed examination of exposure ratios (photon flux/OHexp) that have improved understanding of the potential for photolysis for different species. I recommend examining this manuscript (particularly figures 1 and 2) and discussing the potential for photolysis under your experimental conditions. The calculation for percent interference by photolysis is straightforward and should be performed for any OFR study.
  - e) With OFR-185, HOx recycling can impact OH formation (Peng et al., 2015, Palm et al., 2016). As with OHRext and photolysis, the impact of HOx recycling (the removal of OH through  $\text{H}_2\text{O} + h\nu (185\text{nm}) \rightarrow \text{H} + \text{OH}$ , then  $\text{H} + \text{O}_2 \rightarrow \text{HO}_2$ ) under the experimental conditions needs to be addressed.
  - f) In lines 238-240, differences in the sum of species at different levels of aging are attributed to semivolatile organic compound (SVOC) losses. Did you perform “dark” experiments (i.e., collect particles and gases through the PAM-OFR without the lights on) at any point? Particles and gases collected through the PAM might be subject to different losses compared to those collected before the PAM (Palm et al., 2016). Since you are comparing fresh and aged profiles, which were collected before and after the PAM, respectively, the potential for wall losses needs to be addressed.
  - g) Several estimation equations have been developed to better characterize the PAM-OFR under different operating conditions. The OFR exposures estimator (available for download at <https://sites.google.com/site/pamwiki/hardware/estimation-equations>) is immensely helpful for understanding how different species are expected to interfere with desired OFR chemistry. Estimation equations for LVOC condensational losses for the PAM-OFR are also available on the PAM wiki. I would suggest using these tools to better characterize PAM-OFR operating conditions and citing the sources provided therein.
2. In many places, more discussion of previous work is needed.
- a) In paragraph 2 of the introduction (lines 71-81), chemical profile measurements are discussed in the context of different fresh source contributions, yet the only citation provided is Chow et al. (2002). Please provide similar citations for each of these source contributions.
  - b) As stated above, using a PAM-OFR to study BBOA is particularly challenging. There have been several studies that have improved the community’s understanding of PAM-OFR BBOA oxidation. This manuscript would greatly benefit from further discussion of previous BBOA PAM-OFR experiments to provide further context for results. A few that come to mind include Cubison et al. (2011) and Ortega et al. (2013). Furthermore, to my knowledge, Sumlin et al. (2017) were the first to use an Aerodyne PAM-OFR to characterize both chemical and optical properties for aged and fresh peat BBOA. Given the similarity in fuel type, oxidation method, and scope of measurements, this study would provide useful context for your results in this and future publications (particularly the publication wherein UV/Vis and FTIR measurements will be discussed).
  - c) In line 121, it is more appropriate to cite the first description of the PAM (Kang et al., 2007) and at least the Aerodyne PAM documentation (reference 2 in this manuscript, lines 524-525) rather than your own co-authored publications, unless the PAM-OFR was modified for this study in ways described in Cao et al. (2019). I was able to verify that Watson et al. (2019; published as a discussion paper in ACPD) does not describe any PAM-OFR modifications at this point, and therefore the citations are incomplete. If Cao et al. (2019) describes modifications to the PAM-OFR, this needs to be explicitly stated.

### Technical/Minor Comments:

1. Line 38: Either change “reconfirms” to “confirming,” or change “reconfirms” to “confirms” and remove the preceding comma.
2. Lines 38-41: the use of “intermediate profile” in this sentence is confusing. Consider rewording this sentence for clarity.
3. Line 86: Consider using “improved” rather than “perfected,” as there are still many remaining challenges associated with using the PAM-OFR.
4. Lines 113-116: Please revise this text to make the statement a complete sentence.
5. Line 289: Change the double-dash to a comma.
6. Table 1: Since this table is so long, I would suggest carrying the table column labels across to each page to improve table readability.
7. Figure 6: I would suggest changing the y-axis range to ~70-100 so differences in less-abundant species at the top of the bars are easier to distinguish.
8. Figure S1: The high-oxidation condition is given in the caption as 6.79 rather than 7 (as it is discussed in the manuscript) and should be changed.

### References:

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