

Reviewer 2

The paper by Liu et al. summarizes aerosol composition measurements during the HISCALE project in Oklahoma. Measurements of aerosol composition and trace gases were carried out using a high-resolution AMS and PTR-MS. HYSPLIT backtrajectories were used for source region characterization and positive matrix factorization was used to categorize OA into distinct factors. Since the campaign included a spring and summer segment, authors could contrast the seasonal composition differences. They conclude that overall biogenic VOCs seem to control OA formation. Case studies were explored in more detail to investigate OA formation from biomass burning and isoprene oxidation. Overall the paper is well written and fits the scope of ACP. Discussed seasonality in OA composition and formation pathways are interesting. There are some issues that need further clarification, especially in the assignment of PMF factors and interpretation of those factors. Details are highlighted below.

1. There are many average values presented throughout the paper; it will be useful to also report the standard deviation of the averages to get a better understanding of the variability in the data.

Our response: Thanks for the comment. We agree that averages are not sufficient to represent the variability in data, thus for some of the basic parameters such as aerosol- and gas-phase species, detailed information including averages, median, 25th and 75th percentiles, were listed in Tables 1&2 in the originally submitted version, and in our discussions we provided average \pm stdev for O:C ratios, H:C ratios, etc. (e.g., lines 220 and 222).

For some of the other parameters, the variability were originally illustrated in figures, i.e., the distribution of f44 and f43 (Figure 5), time series of PMF-retrieved factors and their mass fractions (Figures 6&7), and distribution of O:C, H:C ratios for the April 29 event (Figure S10). We have adjusted the texts to also provide the stdev plus average values (please see Lines 167, 169, 192-193, 221, 223, 248, 308, 432, 452).

2. L113: How was the AMS bounce fraction corrected for? Was SMPS data used solely for this instead of composition-based CE? If so, how were differences in upper size cut of the two instruments and density considered?

Our response: The AMS bounce fraction was corrected based on comparison with SMPS data. During HI-SCALE, the SMPS measured the particle size distribution from 14 nm to 710 nm (mobility diameter). The AMS CE drops to approximately 50% at 1 μm aerodynamic diameter, which corresponds roughly to a 700 nm mobility with a reasonable particle density of $\sim 1.4\text{g/cm}^3$. Therefore, the instruments are measuring very similar size ranges of particles. In addition, the comparison between SMPS-determined and AMS-determined aerosol volume concentrations (converted from mass concentrations of various species and composition-based density) showed a relatively constant ratio, as shown in the plot below, suggesting the relative abundance of various chemical compositions did not significantly influence the CE during our campaign.

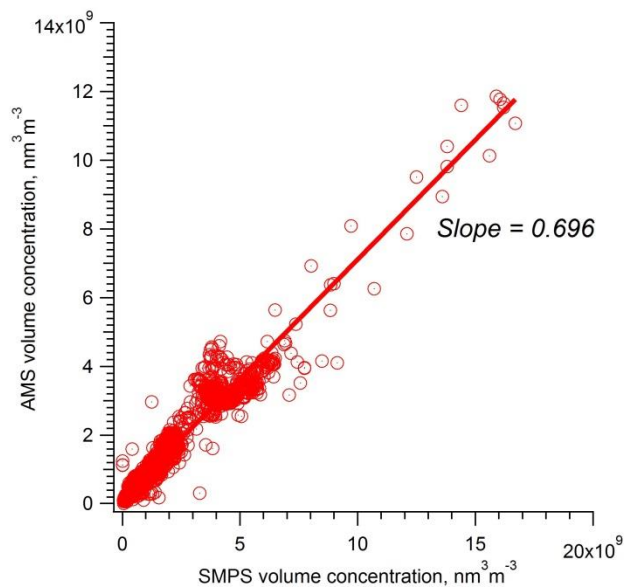


Figure R2. Aerosol volume concentrations determined from AMS measurements compared to measurements from the co-located SMPS.

3. L180-181: what could the source of sea salt be at a region so far from the oceans? The majority of these particles will not make it through long-range transport?

Our response: We have eliminated these lines based on these concerns and the concerns of another reviewer.

4. L198: Another reason for low concentration of aromatics is their higher reactivity during the summer. This should be considered as a possibility.

Our response: We thank the reviewer for this comment. Yes, higher OH concentrations in the summer may also lead to lower concentrations of aromatics. We have added a line to the manuscript with this additional possibility (Lines 205-206).

5. Last paragraph in section 3.2: I find the discussion on oxidation state as measured by O/C, OSc and f44 circular. All of these metrics are different ways to show the same thing and primarily follow the f44 patterns, so the fact that O/C and OSc in spring were higher than in summer and then f44 in spring was also higher is not an additional evidence for increased oxidation state.

Our response: We thank the reviewer for raising this point, but disagree somewhat. OSc is the most complete measure of the carbon oxidation state and clearly it is influenced by O:C, which is in turn influenced by f44. But the H:C ratio also influences OSc and is independent of O:C. Additionally, high O:C isn't necessarily a function of a dominant f44; for example isoprene photooxidation SOA has high O:C yet m/z 44 is not the dominant peak in the spectrum (Liu et al., 2016). Therefore, we feel providing all these measures of the carbon oxidation state are useful for making the point, though perhaps the text is more wordy than necessary. To address the reviewer's concerns, we have shortened and simplified the discussion as follows (Lines 224-228).

“The first possible explanation is that the aerosol in the spring is more aged due to a longer residence time in the atmosphere, potentially different oxidant concentrations, or a combination of both. Photochemical aging leads to an increase in f44, O:C, and OSc, all of which are higher in the spring than in the summer (Alfarra et al., 2004; de Gouw et al., 2005; Aiken et al., 2008; Kleinman et al., 2008).”

6. L245-250: BBOA factor: There's some enhancement in acetonitrile (as shown in SI) during the BB event in Spring. What is the correlation for the time series of BBOA and acetonitrile shown in Fig. S11. Furthermore, peaks in CO seem to correlate with peaks in BBOA factor; I wonder if correlation can be looked at for a subset of times (say when

BBOA factor is higher than a certain amount or the time shown in S11) to have an external verification of the BBOA factor assignment. What was f73 in the BBOA factor? Was the fraction highest in the BBOA factor? If so, then it's circular to identify a factor based on f60 and f73 and show the great correlation of the factor with individual tracers at m/z 60 and 73.

Our response: (1) Regarding the enhancement in acetonitrile in Fig. S11. There was some weak enhancement during the April 29 event, but this was not as clear of obvious as the increase in m/z 60 in AMS spectrum. The correlation between BBOA and acetonitrile is relatively weak, with $R^2 = 0.52$. Following the suggestions by another reviewer, we have added some discussions on the possibility of biomass burning types with lower acetonitrile emissions, such as residential wood burning (Lines 468-471).

(2) During the April 29 event period, CO did show a correlation with BBOA, but also with HOA (please see the plot below, Figure R3). It is reasonable that CO serves as a tracer for both biomass burning and anthropogenic emissions, so it is not surprising that periods influenced by biomass burning also display higher CO. We have added some of this text to the manuscript (Lines 256-257).

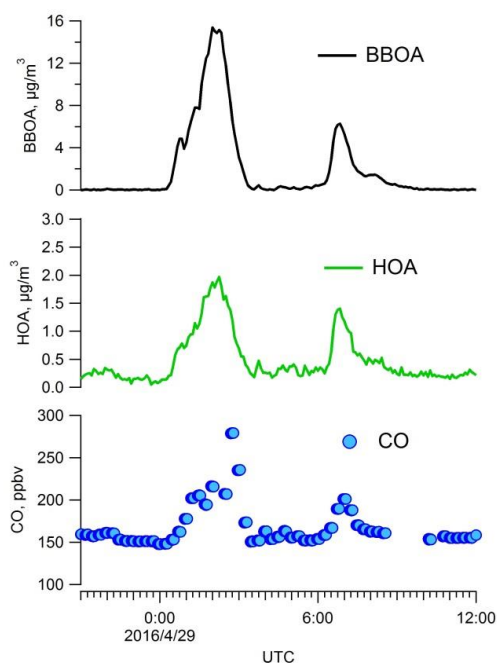


Figure R3. Time series of BBOA, HOA factors and CO concentration during the April 29 event.

(3) The f_{73} we showed here is for the ion of $\text{C}_3\text{H}_5\text{O}_2^+$, which is also a widely used BB emission signature as this ion is related to levoglucosan-like species. The f_{73} is highest in BBOA factor and averaged 6.3‰ in the BBOA factor.

7. Lines 251-261: the poor correlation between HOA and CO could also mean that CO has other sources. Given the influence of biogenic emissions, it's likely that secondary CO production is also contributing to the observed CO concentrations, which would certainly not be correlated with HOA. How is CO correlation with some of the BVOC tracers?

Our response: The poor correlation between HOA and CO could mean CO has other sources, and we have discussed that both BBOA and HOA could contribute to CO, resulting in the relatively weak correlation between CO and a single PMF factor (Lines 264-265 and Figure S5).

We examined the correlation between CO and BVOCs and do not find significant correlations (please see the two plots below, CO correlation with isoprene and monoterpenes, respectively). Therefore the secondary CO production is unlikely an important contributor to the observed CO concentrations.

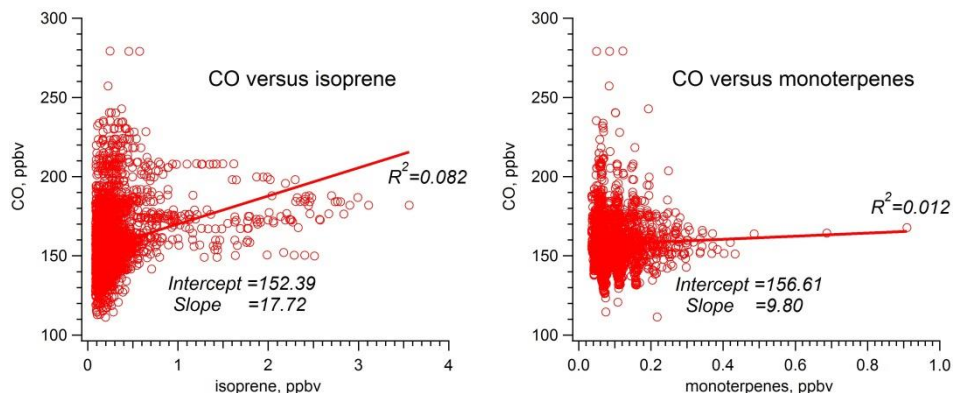


Figure R4. Comparison of CO with isoprene (left) and monoterpenes (right).

8. L259-261: I'm curious if the HR data of the HOA factor includes only the C_xH_y^+ type of ions. Was the PMF run with the HR spectra or UMR? Given the use of HR-AMS, I

assume the former although there's no evidence of HR-type of PMF results. If HR spectra were not used in PMF, please explain why not.

Our response: The PMF was run with the HR spectra. Shown in the plot below, the HOA factor is dominated by the $C_xH_y^+$ family of ions, but also has some contribution from the CHO family of ions. We compared the factor spectra with literature data, and found some previously reported hydrocarbon-like OA factors also include CHO type ions (e.g., Struckmeier et al., 2016; Hu et al., 2018), similar to our PMF results.

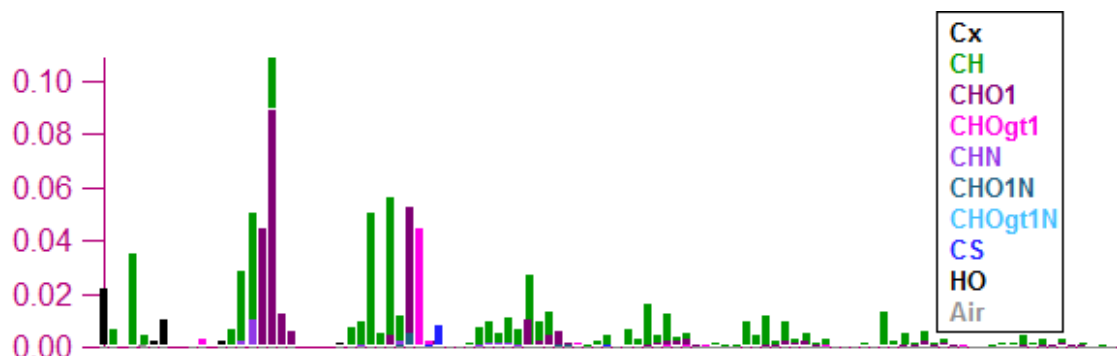


Figure R5. HR spectra of PMF-resolved HOA factor during spring IOP.

9. L284-286: I thought OOA-1 is always the more oxidized type. The separation of OOA factors don't fully make sense to me. OOA-1 in Spring has a higher contribution of m/z 55, 57, etc, and lower f_{44} , yet its OSc is higher than OOA-2. In summer, OOA-1 has a higher contribution of m/z 29, 43, 55, 57, similar f_{44} and lower OSc. It's confusing that in one season OOA-1 is more oxidized and in the other season it's OOA-2. Could it be that the two names are swapped (or one is a typo here)? Could it be that the OOA factors are not 'cleanly' separate from one another?

Our response: Yes, this is a typo and has been corrected. We thank the reviewer for pointing this out.

10. L429-430: If the lifetime of levoglucosan is 2 days, I don't think a significant amount of it would have decayed during a 6 hr transport time (remaining concentration= $\exp(-6/24)$ $C_0=0.88$ of initial concentration). Please clarify. Perhaps you mean the transport time from Canada is longer, in which case that time should be noted here and not 6 hrs.

Our response: Yes, we were referring to the transport time from the Canada fires. We have adjusted the expression accordingly (Line 446).

Refereces

Liu, J., D'Ambro, E. L., Lee, B. H., Lopez-Hilfiker, F. D., Zaveri, R. A., Rivera-Rios, J. C., Keutsch, F. N., Iyer, S., Kurten, T., Zhang, Z., Gold, A., Surratt, J. D., Shilling, J. E., and Thornton, J. A.: Efficient Isoprene Secondary Organic Aerosol Formation from a Non-IEPOX Pathway, *Environ Sci Technol*, 10.1021/acs.est.6b01872, 2016.

Hu, W., Day, D. A., Campuzano-Jost, P., Nault, B. A., Park, T., Lee, T., Croteau, P., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L.: Evaluation of the New Capture Vaporizer for Aerosol Mass Spectrometers (AMS): Elemental Composition and Source Apportionment of Organic Aerosols (OA), *ACS Earth and Space Chemistry*, 2, 410-421, 10.1021/acsearthspacechem.8b00002, 2018.

Struckmeier, C., Drewnick, F., Fachinger, F., Gobbi, G. P., and Borrmann, S.: Atmospheric aerosols in Rome, Italy: sources, dynamics and spatial variations during two seasons, *Atmos. Chem. Phys.*, 16, 15277-15299, 10.5194/acp-16-15277-2016, 2016.