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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Vertical characterization of Highly Oxygenated Molecules (HOMs) below and above a boreal forest canopy" *by* Qiaozhi Zha et al.

Anonymous Referee #2

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The article by Zha et al. touches on important but challenging issues of how the extremely low volatility, highly oxidized molecules (HOMs aka ELVOC) behave below and above the tree canopy. The article is generally clear and makes many confident insights into the atmospheric variability of these molecules. Because these molecules have high propensity to form SOA, such measurements are needed and potentially valuable. However, I would have some important reservations to this version of the manuscript about the data interpretation and QC/QA, but hopefully, this can be successfully addressed by the authors.

Major

1) Two heights were chosen for measurements of HOMs by two different CI-APi-TOF instruments. Although I agree with the other reviewer that this might be regarded as a flaw, I think it does not have to be a critical flaw as long as there is a substantial effort to ensure that the two instruments were in perfect agreement. I am surprised why a portion of measurements was not conducted at the same height (either ground or tower) by both instruments side by side first before moving on to measuring at two heights. It is unfortunate because the collocated measurements would help to ensure that the data reported by two instruments are indeed identical. I am concerned that it might be difficult otherwise to demonstrate this, because there are numerous factors that may affect the agreement between two different instruments apart from the relative transmission. For example, fragmentation, clustering, declustering, or other processes modulated by changes in ambient temperature and humidity may have differed as a function of day, as a function of height, and over longer time scales in either or both instruments. It is therefore really difficult to get convinced if the differences are necessarily because of the height and not because of the differences in each instrument's quantification. A single point laboratory comparison of just the relative transmission of two instruments does not seem sufficient, because of the inability of assessing the factors which change over time. It would be ideal to calibrate regularly the instruments independently and assess separately the deviation from the theoretical transmission of the TOFs like in Heinritzi et al. (2016). Then you could compare the datasets and see how consistent they would be in the middle of a day and at night.

2) Eq. 1 is only valid if the conditions in the reaction chamber or TOF chamber have not changed. Small variations in pressure, temperature or humidity could affect the calibration coefficient. It would be inappropriate to expect that if you set the collision rate the same for all the ions, the relative consistency in two instruments will be the same, because the sensitivity can change over time also because of the drift parameters and resulting issues such as different fragmentation which would not be accounted for by the single transmission correction. It is therefore recommended to take zeros

and calibrations of the instruments frequently and none of these are shown except that permeation device is mentioned.

3) I understand that the authors did not seem concerned about the absolute quantification (L165-166) but even the relative quantification is uncertain if one of the instrument was affected by different conditions or its sensitivity drifted throughout a day. It is unclear how the instruments were housed and if the temperature inside the instruments were monitored and if it was consistent at the two heights. A visual schematic would be useful. One way around could be to either add a period of collocated measurements for a few days and compare the range of compounds or show how stable baselines, sensitivities, and transmissions, were throughout the measurement period if you did regular calibrations.

4) Why do you assume a noon period should have identical HOMs concentrations at two heights? I thought these were the first measurements of HOMs at two heights or can you provide a reference? Again, I am surprised that this period was chosen for transmission comparison instead of collocating the two instruments for a longer period. I am not convinced that it is fair to assume that all the HOMs will have no concentration gradient during a day. I am worried that if the HOMs are lost more rapidly at the surface the relative transmission ratio between the instruments may be biased towards larger masses which could be expected to be lost as a function of mass-dependent volatility which could mimic the duty-cycle and transmission related mass discrimination.

5) Fig. 2 shows a good agreement for HOMs during noon and not so good otherwise. This relative scaling seems rather arbitrary and not completely unsurprising given the data were normalized using Figure 1 which was derived for the noon time. I am skeptical if these differences really represent the effect of different heights. The differences are huge because the data are shown on a log scale. I would recommend showing the comparison on a linear scale.

6) Overall, I was missing a stronger link to chemical and physical properties of HOMs

and a deeper insight into individual classes and not just the total sum of HOMs. In particular, the transport could be molecule specific and may not be unified across the full range of HOM vapor pressures. I feel that the dataset has a much higher potential for teaching a reader about the behavior of HOMs. The current version of the paper gives an impression of semiquantitative and speculative in terms of HOM vertical behavior. I am not convinced by looking at temperature variations (Fig. 2) that the inversion hypothesis is strong. There is much attention directed to the general remarks about advection and turbulent quantities which is difficult to infer how they affect HOMs without direct flux measurements of HOMs by eddy covariance.

Minor

7) I wonder why you are adopting the HOM nomenclature and not ELVOC. Mentel et al. (2015) suggested that the latter is more appropriate when referring to atmospheric impacts and HOMs if the focus is more on compounds' structure. As you are focusing on the behavior in the atmosphere I think considering volatilities could make sense. Are you sure that all the molecules you report are highly oxidized (high carbon oxidation state)? That would not be true for compounds such as cyclic and linear siloxanes which should be subtracted from the HOMs class.

8) Figure 3 does not provide much information when it is colored by the time of day. For the reasons mentioned above the scatter outside of the noon hour might not necessarily be because of less good mixing other than at noon. One could possibly learn more if the data were colored by potential temperature or relative humidity.

9) Figure 4c, the scatter looks weird that it is so much shifted (by an order of magnitude) but still reasonably correlated. I wonder if it is possible to evaluate any volatility dependent difference but it seems that it might be difficult if there is a high uncertainty in transmission differences.

10) Figure 1 is technical and could be moved to SI. I would suggest to replace it

by separate individual curves of theoretical and measured transmissions from each instrument and the datasets should be corrected individually.

Technical

L67 space between ")" and "from".

Table 1, ensure the number of significant figures is consistent and as appropriate.

Table 2, if there is only one N atom in a molecule there is no need to add 1. For example, $C_{10}H_{15}O_{11}N_1$ should be $C_{10}H_{15}O_{11}N$.

References

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