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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Semi-volatile and highly oxygenated gaseous and particulate organic compounds observed above a boreal forest canopy" *by* Ben H. Lee et al.

Anonymous Referee #1

Received and published: 5 May 2018

This paper presents a novel and interesting dataset on oxidized organic species contributing to both gas and aerosol phase organic aerosol in a remote boreal forest. The analysis is possible by use of a FIGAERO inlet to monitor gas and aerosol phase separately but using the same I- mass spectrometer, and positive matrix factorization to sift the complex spectra into 3 primary factors with unique diel behaviors. The authors interpret their results as showing a strikingly (considering the remote location and low NOx) large contribution of particulate organic nitrate to the organic aerosol mass concentrations, especially at night. This is consistent with other recent work and thus builds evidence for an increasing role for organonitrates in SOA production. This paper is likely to be of great interest to the SOA research community and I recommend

publication following minor revisions.

General suggestions: 1) since you will ultimately compare the org nitrate contribution to results from Kiendler-Scharr et al around Europe, and SOAS, I suggest to include somewhere in your introduction the average NOx concentration and BVOC composition (is it exclusively a-pinene?) at Hyytiala. Then when you discuss the surprisingly large nitrate contribution, you can point to the differences.

2) in the methods discussion, it sounded like you only ran PMF on the gas phase data. But I think you may have separately done both gas and aerosol? Or did you just use the same groupings as found by the gasphase PMF for both phases to make the later plots? Either way, please clarify in the text.

3) Why does your analysis only include zero or one nitrogen per molecule? Were no molecules with two or more observed, or did you omit them from the analysis?

4) The discussion of variability in figures 6 b and d serving as evidence for the short lifetimes of some species was confusing to me. I don't see significantly greater variability in those figures compared to e.g. daytime gON in panel a.

5) what is the difference between positive matrix factorization and non-negative? Maybe add a line to the methods explaining the difference and why you chose the latter.

6) can you account for the effect of boundary layer height changes, to help interpret the morning nitrate source?

7) it looks like there is higher pON during the hottest days of your study. Can you comment on this? Can temperature-dependent partitioning be ruled out in explaining any of the diel variation? (Also around p. 8 line 5)

8) P.6 around line 15 you state the yield must be less that 0.5 to explain decreasing Abundance with # of oxygens. Does this assume that whatever does not yield functionalization stays at the same O:C?

9) Does figure 6c mean there is no nighttime o3 chemistry? If all gas phase OC is in the daytime factor? Or is the nighttime factor actually just a nitrate factor and o3 chemistry would be grouped in the daytime OC factor even if there is some at night.

10) figure 7: are the nighttime factors so much sparser MS because there's no autooxidation in there, since nitrates don't need that to be condensable enough?

Minor technical edits: Abstract line 22: mention that this comparator site is in the SE US.

Top of p. 3: suggest to remove the last line of the intro, so you end with the statement of what you add with this work.

P. 4 line 8: " as it is of order a factor of 2"

Line 11: " and the interpretation of these observations"

P. 5 line 7: "approach is that species exhibiting subtle differences...trends may be lumped into"

Line 22: are you talking about levels greater than expected in the particle phase specifically? Clarify

P.6 line 29 " motivates the use of"

P.7 Line 4 and elsewhere: "adhered to" sounds strange to me - how about belonged to?

Line 21: "imply that formation rates.... were sufficiently higher...during the day, consistent with modeling results specific to the SMEAR"

Line 27: "accumulated in the nocturnal "

P. 8 line 10: is the Yan study referenced at the same site & season? Or similar forest type? Suggest to add additional comment specifying, and then in the next lines clarify which study you mean when. "...summer of 2014 reported here observed most

gaseous...whereas those previous measurements near the canopy floor.. summer of 2012 had observed "

P. 9 line 4: I thought nN previously signified average number of and per molecule ? Different meaning here?

P.10 lines 30 and 32: $\sim$0.35 and $\sim$5%: make both fractions or both percents

Line 31" However, in that study the pON"

P.11 1 " BAECC were also consistent with other observations of unexpectedly high..."

Line 6 "was greater above the more pristine"

Around line 25 I'm wondering about the monoterpene distribution & diel cycle at hyytiala

P. 12 line 9 I'm wondering how you assessed the role of boundary layer dynamics

Line 15: ... or difference bvoc mix making sources different, or different temperatures ... might end this is a little more open ended about explanation?

P. 18 table 1: why is only gOC average mixing ratio reported in the caption?

Fig. 1 : why different units on panel b than elsewhere (ng m-3)? Do I interpret the righthand panels correctly to say that all dimer species are more abundant in the gas phase than particle? This seems surprising...

Fig. 2 : are these all gas phase only data?

Fig. 8: explain the "adjustment" a bit more – is this just no3 mass x 265/62?

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