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Interactive comment on “Atmospheric submicron aerosol composition and particulate organic nitrate formation in a boreal forestland–urban mixed region” by L. Q. Hao et al.

Anonymous Referee #2

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This paper describes aerosol mass spectrometer (AMS) measurements and source apportionment using positive matrix factorization (PMF) made during fall in a boreal forest region which had moderate impacts from various local pollution sources. Submicron aerosol was half organics, a quarter sulfate and the remainder nitrate, ammonia and black carbon. PMF results showed ~90% percent of organics was oxidized organic aerosol (OOA) with a small contributions from hydrocarbon-like organic aerosol (HOA). In addition to including the standard practice of including explicitly organic ions in the AMS PMF analysis, the NO⁺ and NO₂⁺ ions, which can be from both inorganic nitrate and organic nitrate aerosol components as seen in the AMS, were included. This

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produced a forth factor which was almost purely representative of inorganic nitrate. One-third of the NO_x and NO₂⁺ ions were apportioned to the one of the OOA factors, the semivolatile one (SVOOA), indicating that organic nitrates are at least one component of the SVOOA and related to its formation. It is hypothesized that the organic nitrate, peaking at night to early morning, may be produced from NO₃ radical + biogenic VOC -initiated reactions. Several hypotheses are presented as to why the OOA contribution is so large, particularly compared to other measurements in the region.

The manuscript is generally well written and describes a clear and straightforward analysis of AMS/PMF results in an important environment (boreal forest with anthropogenic influences). The authors demonstrate the ability to expand the capability of AMS/PMF to quantify contributions of organic nitrates and their association with organic aerosol sources or processes. This manuscript warrants publication in ACP after relatively minor revisions.

General comments followed by a detailed list of comments are below.

General/Main Comments:

- Two key numbers, SVOOA and LVOOA contributions to OA appear to be grossly inconsistent in the text and figures on which a major conclusion rests (anthropogenic contribution to OOA). It raises concern that other mistakes may have been made in the analysis and interpretation that are not so transparent.

- The authors appear to have overstated/overinterpreted the tenuous conclusion that because there is more SVOOA compared to LVOOA compared to measurements at a more remote location, that all the “extra” SVOOA comes from anthropogenic emissions. While an interesting speculation, the evidence doesn’t warrant the level of certainty that the authors appear to place on it. The authors need to provide stronger evidence in their analysis otherwise assign a more appropriate level of certainty (probably doesn’t belong in the conclusions, at least in present form). See more detailed comments on this aspect below.

- Throughout the manuscript articles are often omitted or inserted incorrectly. Best to have a native English speaker proofread before submitting, if needed.

Detailed Comments:

P17265, L12: delete “the”

P17266, L7-9: Suggests adding “may” before “enhance biogenic emissions”. Most of these studies provide evidence that this appears to be happening, but rarely, if at all, is the evidence demonstrative.

P17266, L20-21: Why cite only older studies showing that quantifying organic nitrates is challenging but not mention more recent studies where it has been done well in the field (e.g. Rollins et al. Science 2012, Liu et al. JGR, 2012, Fry et al., ACP, 2013)? Omitting them appears as cherry picking, ignoring more recent advances in detection of particle-phase organic nitrates.

P17267, L9: need “the” before “city”

P17267, L25: Provide reference for SQUIRREL and PIKA No one outside the AMS community would know what these are.

P17268, L6-8: Why was $CE=0.5$ chosen? Why not use the Middlebrook et al. (AS&T, 2012) chemical-dependent CE algorithm? What was the slope of the AMS vs SMPS after a constant $CE=0.5$ was applied (Fig. 2c seems to show that sometimes the AMS is high and other times the DMPS is higher). Does applying the chemically-dependent CE improve the correlation coefficient? Also, the application of CE correction is for particle bounce on the vaporizer only, not for the lens transmission. For a properly-aligned lens, the transmission should be 100% between ~ 50 -600 nm and then decrease outside that range. So accounting for lens transmission effects would be a size-dependent correction. See Middlebrook et al. for discussion and references.

P17268, L27-29: What happened for the 4-factor solution? It seems equally relevant to comment on that as for the problem with the 6-factor solution (especially since the

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5-factor solution was combined to 4 factors).

P172670, L4: missing “the” before “northern direction”.

P17270, L5: Note the typical durations of the high sulfate peaks (can’t tell from Fig. 2)

P17270, L11: “Pearson’s”, not “Person”; Also, please report the slope too.

P17271, L1: “Major aerosol mass” is vague and should be reworded to clarify what is meant.

P17271, L2: Need “the” before “paper mill”.

P17271, L13: “The cycle [of sulfate] does not display dramatic variations” is a bit strong language as it’s very much an understatement. There is very little average diurnal variation so better to state from that angle.

P17271, L20: Add “a” before “similar”. There are several instances throughout the manuscript where articles (the, a) are left out or included when not needed. I’ll leave it up to the authors or ACP to carefully proofread and correct these and will not list them all here.

P17271, L28: “observed to distribute around a peak in the northwest direction” is odd wording. Consider rewording.

P17271, L29: “which is believed to be due to emissions from the paper mill”. Give a reference for this or explain reasoning.

P17271-72: Why is the diurnal cycle of sulfate discussed here but nothing about the other species? Seems incomplete (even if there is more detailed discussion of nitrate later).

P17272, L3-9: In investigation/discussion of the ammonium balance and acidity it would be appropriate to exclude the organic nitrate fraction of the total AMS-measured nitrate. It probably doesn’t make a lot of difference since sulfate is » nitrate but nonethe-

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less this point should be made here since the authors have this information.

P17273, L13-15: Showing a high correlation of the HOA factor with the saturated m/z 57 ion peak doesn't really seem meaningful, in that, if all the m/z 57 was in the HOA factor, clearly one would expect them to correlate. Pointing out that the HOA factor looks like other HOA factors and combustion spectra would be more relevant and convincing. Correlation with other combustion factors such as BC would also be more relevant to the discussion. Also, correlation with NO_x is weak. Can the authors comment on that?

P17274, L24: Sentence doesn't make sense (non sequitur). What is being compared?

P17275, L2: "are representative of SOA" is unclear. Elaborate.

P17275, L11: "SVOA and LVOA components account for 65.7% and 23.9% of the total organic aerosol mass". Looking at Figure 8A, it appears the average SVOOA is ~0.6 ug/m³ and LVOOA is ~0.45 ug/m³ which means that SVOA is only 30% higher than LVOOA. Yet the percentages in the text suggest it's 2.7 times higher? Discussion on the following page and a statement in the conclusions is based on these percentages. This is a bit worrisome since while this apparent error is obvious to the reader, it raises the concern that there are other major calculation errors that are not possible for a reader to discern.

P17276, L1: change "approximately" to "approximated" and "in" to "at the"

P17277, L6: "component" should be plural

P17277, L7: "one more HOA factor"? Do the authors really mean "one more factor, which was a HOA factor"?

P17277, L10-12: The authors have concluded that urban emissions "contributed more than 40% of OOA species by mass" based simply on comparing the SVOOA contribution to the LVOOA contribution and that to the relative ratio at a more remote site in the region and then assigning the "extra" SVOOA to SOA from anthropogenic SOA. This result also appears in the conclusions (apparently adding in the HOA to get the total

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contribution of anthropogenic OA to total OA of 50%). The authors give several other reasons in that section why there may be high OOA mass fraction during this study, e.g. anthropogenic-biogenic interactions, cooler temperatures, etc. (pages 17275, 17276). In fact, looking at the wind roses in Fig 7A, it appears that SVOOA is a larger fraction of OOA when the wind is from the northern wind sector hemisphere rather than from the south of southwest where the urban center is. It is not clear why the authors have picked this particular one out as the explanation that they seem to assign considerable certainty (i.e. repeated in end of section and conclusions). The reasoning and support for this is tenuous at best (albeit certainly possible). Other reports of anthropogenic-biogenic interactions appearing to show enhanced SOA typically have shown that most of the carbon is modern, not fossil. It seems unlikely that ~50% of the carbon was of fossil origin at this site (which this claim would suggest). It would seem more appropriate for the authors de-emphasize this one particular possible explanation for their observations, probably giving it equal weight to the other 6 possibilities presented in Section 3.2.2. Unless, of course, they can present more convincing support.

P17278, L27-28: Authors state: “organic nitrate shows a good correlation with SVOOA, suggesting that it could be semi-volatile” Like the m/z57 correlation with HOA (see above), this statement seems a bit circular or indirect logic. 75% of the organic nitrate has been attributed to the SVOOA PMF factor (Fig 9) so clearly we’d expect them to correlate. Isn’t the fact that 75% of the organic nitrate is in the SVOOA factor the most direct evidence that it may be semivolatile? Likewise, don’t the results suggest that 25% is not SV?

P17279, L13: add “been” before “observed”

P17280, L5: I think the authors mean organic nitrate “fractions of nitrate”, not “concentration” based on the preceding discussion of other observations.

P17280, L6: Should qualify as organic nitrate “functional group” since technically the whole molecule is an organic nitrate which is not what is reported here.

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P17280, L18: It doesn't seem useful to report the total contribution of the highest two species (organic and sulfate) since that is a common result and they have very different sources. Reporting their contributions separately would be more informative. Ditto for abstract. Same goes for the 89.6% for SVOA + LVOOA a few sentences below (but in that case also noting that together as OOA they comprise 90% of the OA mass may be appropriate).

P17281, L6: delete "as"

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 17263, 2014.

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