

Interactive comment on “Physicochemical properties and origin of organic groups detected in boreal forest using an aerosol mass spectrometer” by T. Raatikainen et al.

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We would like to thank referee #1 for constructive comments. Additional calculations about AMS data analysis, PMF, growth factor correlations and diurnal cycles will be shown in supplementary material. Responses to specific comments are below.

Specific Comments:

P21848, L13: "...OOA1 is the less volatile and hygroscopic organic group..." It should be unambiguously stated that OOA1 is the more hygroscopic component at C10346

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this instance (abstract!)... Otherwise, the hurried reader might think that "less" also refers to "hygroscopic" - this would be against the intuition as OOA1 = more aged = more oxidized = higher polarity = higher affinity towards H₂O and is at odds with the conclusions drawn further below in this paper. Furthermore, the classification on P21869, L1 ("OOA1 is]... fairly hygroscopic...:") is confusing as fairly can mean "more or less" but also "pretty well".

We will modify the text as "OOA1 is the less volatile and more hygroscopic organic group" (page 21848) and "OOA1 species are less volatile and more hygroscopic" (page 21869). In addition, it will be mentioned that OOA1 and OOA2 are equivalent to LV-OOA and SV-OOA in a recent paper by Jimenez et al. (Science, 326, 1525-1529, 2009).

P21848, L20: ("...other seasons...") and maybe also different types of sites. ...

This sentence will be reformulated

P21849, L2: I would generally not consider chloride and sodium as main fractions of (non-refractory) PM₁. If this is different for the Hyytiälä site, please add these components (or at least Cl⁻) to Figure 1.

Sodium and chloride will be removed from the list as these are not common in Hyytiälä.

P21849, L18: I suspect the referenced Hock et al.-paper does not contain a plausible identification/verification of ambient OOA1 and OOA2 as identified in this manuscript. E.g. the correlation OOA1 vs. sulphate or OOA2 vs. nitrate was not shown. More-

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over, the reported ratio OOA1:OOA2 is at about 1:2 therein, which is at odds with OOA1:OOA2 ratios found at other sites by the PMF-AMS method. Please remove this citation or explain why you think this work includes a good example for OOA1 as a low-volatility OA component and OOA2 representing a semi-volatile OA component. Further in the paper you too mention that OOA1 and OOA2 found therein is rather unusual (P21858, L3: "...but Hock et al. (2008) found the opposite diurnal cycle as if their OOA2 species were less volatile..."). I think 'OOA1' and 'OOA2' have a different meaning in the Hock et al.-paper and should not be cited in that context.

Hock et al. (2008) used different factorization method (MCA), which means that the results may not be fully comparable. Therefore, this reference is changed to Ulbrich et al. (2009). For the same reason, reference to Hock et al. (2008) is removed from pages 21857 (L20) and 21858 (L3-4).

P21850, L4: "the AMS can detect the above mentioned species." - agreed, but only the non-refractory portion, e.g., sulphate from refractory components (K₂SO₄) can not be fully transmitted from inlet to detector. Please specify... .

"With the exception of elemental carbon, potassium and sea salt, the AMS can detect the above mentioned species" will be changed to "With the exception of potassium and species from refractory material such as elemental carbon, metal oxides, fly ash, crustal material and sea salt, the AMS can detect the above mentioned species (Canagaratna et al., 2007)"

P21850, L9: "...growth factors are highest during days"... this does not apply to both EGF and HGF. Please be more specific...

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"growth factors" in line 9 will be replaced by "they"

P21853, L11: "This was also confirmed in our laboratory experiments." - what was the type of lab experiments you conducted?

Results of the experiments on mixed ammonium sulphate- α -pinene particles were not changing when the residence time was increased. This will be mentioned in the updated version.

P21854, L17-18: add a reference to support this statement

Reference to Seinfeld and Pandis (2006) will be added.

P21855, L12: What do you mean by "charge balance" here? Does this mean you a priori assumed that NH_4^+ and K^+ balance the negatively charged anions (NO_3^- , SO_4^{2-} , Cl^-) and the RIE of NH_4^+ was adjusted accordingly? Please explain.

Yes, this is what we would expect. Ammonia RIE is known to vary between 3.5 and 6.0 (at least), and this charge balance approach is one way to find a suitable value. This will be explained in the text.

P21856, L9: Question: was m/z 44 down-weighted as well or not? According to the findings reported in this and other papers, m/z 44 mostly represents aged and low-volatility reaction products and its time series points to a regional, stable organic background pollutant. PMF assumes non-reactivity / constant factor profiles over time, which I guess is fulfilled most closely for m/z 44 or OOA1 species and hence

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m/z 44 should be 'up-weighted' rather than down-weighted. PMF users should keep in mind that not only instrumental uncertainty but also modelling uncertainty needs to be considered, which has been neglected in some precedent PMF-AMS studies. This error should not be repeated here and I would expect - in case that such type of down-weighting was performed - that the authors repeat the PMF-AMS calculations w/o down-weighting m/z 44 and detail the differences in the PMF results.

M/z 44 was down-weighted as suggested and justified by Ulbrich et al. (Atmos. Chem. Phys., 9, 2891-2918, 2009). This downweighting of m/z 44 (and m/z 41) is now explained in the supplementary material. Briefly, m/z's that are calculated from other (measured) m/z's should not be included in the PMF. If these are included, they upweight the measured values, as described in Ulbrich et al.

P21856: L16-17: If you can clearly state that reasonable PMF results were found for FPEAK = 0.0 ... -0.3, then I would expect that you use this range to infer worstcase uncertainties for the PMF-AMS method as done by Allan et al. (2009; ACPD: www.atmos-chem-phys-discuss.net/9/19103/2009/).

The FPEAK range is open to interpretations, but for the current FPEAK range the average OOA1 mass fraction is (48+/-1)%. This seems to be quite small worst case uncertainty. Furthermore, some readers may understand this as an uncertainty for the average mass fraction. As organic composition varies a lot, standard deviation for the average OOA1 mass fraction is 23 %. Therefore, differences between the selected and the extreme FPEAKs are discussed only in the supplementary material.

P21857, L12-15: Please calculate and report the average ratios m/z 57 (tracer for fresh emissions) vs. total OA conc. and m/z 60 (tracer for wood burning) vs.

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total OA conc. for this campaign. Low ratios would support the fact the HOA and P-BBOA can not be retrieved by FA-AMS as it is also possible that e.g. HOA and OOA2 are correlated and therefore non-separable by means of PMF and a different approach would be necessary (e.g., Lanz et al., 2008, Environ. Sci. Technol.; <http://pubs.acs.org/doi/abs/10.1021/es0707207>).

Average ratios of m/z 57 (1.1 %) and m/z 60 (0.2 %) to total OA will be reported. It is possible that HOA is e.g. 5 % of the organic mass, but this means that HOA has a negligible contribution to the growth factors and particle volatility. As a result, fitted growth factors could be meaningless. Similarly, strongly correlated mass concentrations, even if they were higher than 5 %, would cause problems in the growth factor correlations. This is clarified in the supplementary material.

P21857, L25: replace "non-volatile" by "low-volatility"

Will be replaced

P21858, L6: "...m/z 44 peak depend..." - very likely you meant that the m/z 44-peak in OOA_x would depend on...

Will be corrected

P21858, L21: The observation of a partially good correlation between OOA2 and NO₃- (I would write NO₃- in case you refer to the AMS-nitrate species rather than gas-phase NO₃(g)) is not very surprising as nitrate and semi-volatile organics have different sources and are subject to different removal processes (and this might be

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even more important for the local NO₃-/OOA2 than for the regional OOA1/SO₄2-).

We agree that it is not surprising that OOA1 is more correlated with NO₃⁻ than OOA2. Charges will be added to nitrate, sulfate and ammonium formulas.

P21859, L3-4: These calculations are crucial for the conclusions of this paper. Therefore, the fitting models / correlations need to be represented by explicit equations, which will be helpful for the readers. At this stage, it might be a bit confusing with respect to what was fitted to what, what quantities were measured/predicted or modelled exactly. What are the numeric values of the fitting parameters and their uncertainties?

Calculations will be clarified in this section as well as in the other specific sections (3.2.1 AMS data and 3.2.2 VTDMA data, which will be renamed). Uncertainties of the fitting parameters (standard deviations) are now added to Tables 2-4.

P21859, L7: Please choose a more specific title for this subsection.

The new title will be "Growth factor correlations based on AMS data". Similarly, title of subsection 3.2.2 is changed to "Growth factor correlations based on VTDMA data".

P21860, L1: "fitting method" - please specify the different fitting methods here.

"fitting method" will be changed to "the above-mentioned considerations such as density and speciation of the species". These will be explained in the supplementary material.

P21864: L15-19: very similar daily cycles for OOA1 and OOA2 were found by Lanz et al., 2007.

Reference will be added.

P21864, 20-21 sqq.: "...but the best explanation is based on changing mixing layer height." The authors' argument (diurnal variability of PBL height) in explaining OOA2 cycles is also applicable to other organic compounds as well. Dilution and concentration via changes in the PBL height act equally (as a first approximation) on all pollutants. In my view, this is not a specific mechanism which might explain the OOA2 cycle exclusively. In contrast, I assume that daytime production of OOA2(g) is enhanced compared to night-time OOA2(g) production as photochemistry outweighs NO3-chemistry (or is there a reason to assume the OOA2 is continuously produced?), whereas colder temperatures at night favour OOA2(g)->OOA2(aer) transitions. This should also be considered to a larger extent when OOA2 cycles are explored. For these reasons, I am not convinced that PBL-height changes are the "best" explanation for the observed OOA2 cycles and the statement should be either toned-down or supported by further evidence. The same comment correspondingly applies to P21869, L17 sqq.

It is likely that the observed diurnal cycle depends on several factors, but we can not show which one is the most important. Therefore, we will just give some possible explanations. Dilution is one possible explanation, because it is important for unmixed species only (OOA2). When OOA2 concentration increases in the evening (from 18:00 to 24:00) ozone concentration decreases from about 46 ppt to 41 ppt, which is not very large decrease (note that in Finland, a large fraction of ozone is long-range

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transported). It is therefore possible that OOA2 is produced during the evening as well.

Corrections:

P21848, L15: I am not a punctuation expert, but maybe it should read here: "The other, less oxidized organic aerosol group..."

Will be corrected

P21850, L21-22: Maybe "Such analyses have been..."

Will be corrected

P21851, L1: "backtrajectories", replace by "back trajectories" (optional)

Terms "backtrajectories" changed to "back trajectories"

P21858, L6: either "...peak depends..." or "...peaks depend..."

Now "peaks of the OOA groups depend"

P21863, L3: "over predict" might be replaced by "overestimate"

Will be corrected

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