

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

Anonymous Referee #1

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General Comments:

The manuscript by Raatikainen et al. presents atmospheric measurements during an intensive field campaign in Northern Europe (Finland) at a boreal/remote site in 2005. The authors investigated hygroscopicity, mass fragmental composition and concentration of the organic aerosol, origin of the aerosol etc. Many interesting conclusions were reached, e.g., they found that hygroscopic growth (derived from DTMA measurements) concurs with the prevalence of a highly aged AMS organic aerosol type as retrieved from the combination of AMS measurements and PMF modelling (PMF-AMS). In contrast, high ethanol growth factors need to be associated with a less-oxidized

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and more volatile OA component. These and other findings represent new insights into the physicochemical properties of ambient OA and are worth a discussion in this forum. I think the manuscript is well-written, well-structured and the conclusions are overall valid. The language is mostly concise, making the paper accessible for relative outsiders.

Some additional calculations with respect to AMS, PMF-AMS, and the comparison of PMF-AMS results with HGF and EGF are needed. It might also be interesting to see some basic mathematical PMF diagnostics, e.g., included as a supplementary material. However, the very nice agreement with precedent studies and PMF-external data leaves no doubts that the PMF-AMS analysis was most useful here and indeed yielded atmospherically relevant results (which is of uttermost importance as such statistical approaches are per se blind to natural science). The following comments and questions are designed to guide the revision of some aspects of the manuscript. After these minor to moderate revisions, it should be accepted as an ACP paper and published rapidly.

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 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".

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

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 compo-

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nents (or at least Cl-) to Figure 1.

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. Moreover, 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.

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. . . .

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

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

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

P21855, L12: What do you mean by "charge balance" here? Does this mean you a priori assumed that NH₄⁺ and K⁺ balance the negatively charged anions (NO₃⁻, SO₄²⁻, Cl⁻) and the RIE of NH₄⁺ was adjusted accordingly? Please explain.

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

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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 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.

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

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. 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>).

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

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

P21858, L21: The observation of a partially good correlation between OOA2 and NO $_3^-$ (I would write NO $_3^-$ in case you refer to the AMS-nitrate species rather than gas-phase NO $_3$ (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 even more important for the local NO $_3^-$ /OOA2 than for the regional OOA1/SO $_4^{2-}$).

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?

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

P21860, L1: “fitting method” – please specify the different fitting methods here.

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

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.

Corrections:

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

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

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

P21858, L6: either “. . .peak depends. . .” or “...peaks depend. . .”

P21863, L3: ”over predict” might be replaced by “overestimate”

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 21847, 2009.

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