**Atmospheric
Chemistry
and Physics
Discussions**

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 #2

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This paper presents the application of PMF to AMS data taken at the Hyytiälä field
station and compares the outputs with various tandem DMA instruments and back tra-
jectory analysis. This is a highly relevant and useful paper because this combination
allows much more detailed insights to be made regarding the organic particulate frac-
tion. In addition, because the field site, the individual instruments and data analysis
techniques are all already well established, this will assist in the advanced interpreta-
tion of past and future datasets. I therefore recommend the paper be published in ACP
subject to the following comments:

General comments:

Generally, the authors should exercise caution in making a priori assumptions as to the
sources and nature of OOA1 and OOA2. While these are starting to become a common
feature in the AMS literature, it is by no means a given that the same behaviour can
be expected at each measurement site. The authors do present a robust case for their
interpretation of the natures of these species, but this should be a discussion point, not
part of the initial explanation of the results. An example of this is given in the specific
comments.

The discussion on page 21856 regarding the choice of FPEAK value is currently in-
adequate. The authors need to describe what they mean by 'reasonable factors' and
'very similar concentration time series' in a much more explicit and defendable manner,
with figures and/or statistics quantitatively describing the reasons for their choice. This
could potentially be included as supplementary material if it risks cluttering the paper.

Throughout the paper, the authors choose mainly to treat the inorganic fraction (am-
monium, nitrate and sulphate) as a single entity. The benefits of this approach are not
very clear and it is even possible that it is actually hindering the interpretation and be
the source of discrepancies such as that reported on P21862, L21. For instance, the
growth factors and volatilities of ammonium nitrate and ammonium sulphate are well
characterised and known to be different, so it would follow that the TDMA fits would
be improved if they were to be handled separately. Additionally, it is also known that
sulphate becomes more hygroscopic and volatile if it is not sufficiently neutralised by
ammonium. I would recommend performing the analysis with the different inorganic
fractions separated, if only to see if it affects the results or not.

The favoured interpretation for the diurnal cycle of OOA2 given on P21864 is flawed;
mixing volume is only a reasonable explanation if there is continuous production of SOA
from VOCs at night. Given that the main processes for SOA production are thought to
be photochemical, this does not seem to be a reasonable assumption. The alterna-
tive explanation given on P21864, that it is the temperature-modulated partitioning of
semivolatile organics, is much more believable, especially given that OOA2 is shown

to be of low volatility in the previous section.

The use of population data in conjunction with HYSPLIT back trajectories is an interesting technique, however as the authors point out, this does not include dispersion, so as a result it can only be used as a qualitative indicator. For this reason, the numerical fitting described on P21867 and shown on figure 8 is not appropriate and the inferences regarding background concentrations are inherently unsafe. A better method would be the use of a model that includes a treatment of dispersion such as FLEXPART or NAME, although this would entail a much more substantial amount of work. An alternative would be to try comparing the data with an intermediate-lifetime gas phase pollution tracer (such as CO). This would not be as powerful, but could conceivably be a more quantitative indicator of anthropogenic influence over an airmass' lifetime.

Specific Comments:

P21848, L18: The phrase "on the other hand" is a little chatty and informal. Suggest rewording.

P21848, L26: I suggest removing the reference to surface tension. While it is hypothetically possible that this is important in the atmosphere, it is by no means established scientific fact.

P21849, L21: References to other papers describing the spring 2005 intensive campaign should be given here (e.g. Kulmala et al., 2008).

P21850, L11: It may seem obvious to someone familiar with this aspect of the science, but the physiochemical reason for the differing solubilities (i.e. polarity) should be mentioned.

P21851, L22: The humidities that constitute 'dry' should be stated.

P21853, L22: The medium used in the absorber tube should be stated.

P21855, L11: A reference to the volume comparison with the DMPS should be given

here.

P21855, L20: The 43/41 peak ratio assumed should be stated.

P21855, L21: The nature of the adjustment should be described.

P21856, L8: The 'default parameters' are mainly specific to PET (not PMF2) and should be stated.

P21857, L25: The authors should be careful to state that the descriptions of OOA1 and OOA2 given are those reported in previous studies and are not necessarily universal.

P21859, L24: The source of these densities should be cited.

P21860, L11: Again, a mention of the relationship between oxidation and polarity should be given.

P21861, L3: Could the charring of organics be a potential source of refractory material?

P21863, L1: Are there any instrumental records of these fluctuations?

P21885: The basis of the predictions shown should be briefly mentioned.

P21886: The method used to estimate volume fractions should be referred to in the caption, as it is not measured directly.

P21887: Error bars indicating the range of variation (e.g. quartiles) would be informative.

Technical Corrections:

P21849, L4: "Hundreds" is a bit of an understatement.

P21850, L3: Does the '5%' refer to the EC or all of the rest of the components?

P21851, L12: Replace 'slightly above 20000' with something more precise, such as the upper and lower estimates.

P21852, L24: Technically, equation (2) is not the ZSR equation but rather a relationship specific to aerosols that can be derived from it.

P21853, L25: The source of the transmission efficiency correction should be cited.

P21855, L21: Correct 'lenses were' to 'lens was'

P21856, L15: Correct 'Two-factorial' to 'Two-factor'.

P21857, L6: The mention of summer time is not needed.

P21857, L7: 'with sawmill' should be 'with a sawmill'.

P21858, L10: The authors should make it clear that the O:C ratio is an estimate, not an explicit measurement.

P21864, L12: Are the diurnal cycles reported means or medians?

P21859, L24: Units of g/cm3 are more conventional for reporting for particulate densities.

P21878: Giving both r and r2 values is somewhat redundant. It is also more intuitive to present the correlations as a matrix.

P21888: Suggest thicker lines for clarity.