Atmos. Chem. Phys. Discuss., 9, C10356–C10365, 2010
www.atmos-chem-phys-discuss.net/9/C10356/2010/

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.

T. Raatikainen et al.

tomi.raatikainen@uku.fi

Received and published: 1 February 2010

We would like to thank referee #2 for constructive comments. Responses to comments are below.

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.

It is true that these OOA species are not well-defined chemical substances (as e.g. NaCl is) and this will be mentioned in the introduction. In the paper they are considered as if they were real chemical substances. This is mainly because we want to give credit to the original papers presenting these groups. Of course, much more work is needed so that these groups could be considered to be comparable to well-defined compounds.

The discussion on page 21856 regarding the choice of FPEAK value is currently inadequate. 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.

PMF analysis will be described in the supplementary material.

Throughout the paper, the authors choose mainly to treat the inorganic fraction (ammonium, 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

ACPD
9, C10356–C10365, 2010

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 justification for not considering separate ions will be given in the supplementary material. The main reason is that the inorganic species have low (rarely above 0.2) volume fractions, so they can not have significant effect on growth factors. In addition, volume fractions are strongly correlated.

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 alternative 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.

This question is addressed in the reply to reviewer #1 comments. Several possible reasons will be given.

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

ACPD
9, C10356–C10365, 2010

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.

FLEXPART and NAME are likely to be more accurate methods, but this is not the focus of our paper. Average air mass origin and population density are just used to show that long range transport and anthropogenic emissions are important for OOA1 and for the inorganic species, but not for OOA2. The numerical fitting is mainly to guide the eye, so a caution for interpreting the parameters will be added.

Specific Comments:

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

"on the other hand" will be removed

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.

It will be removed

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

ACPD
9, C10356–C10365, 2010

References will be added

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.

The polarity explanation will be given

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

These will be given for the three TDMA instruments (<3 % for the OTDMA and VTDMA, and <15 % for the HTDMA).

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

This will be given

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

Volume comparison will be shown and explained (in context with the non-standard instrument adjustments) in the supplementary material.

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

ACPD

9, C10356–C10365, 2010

It will be written that 41/43 peak ratio is 0.8

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

These will be explained mainly in the supplement

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

PMF will be fully explained in the supplement

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.

It will me mentioned in the introduction that OOA1 and OOA2 may not be universal. Because our results about OOA age, oxidation and origin are in good agreement with the previous ones, we are not trying to say that we are presenting new organic groups.

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

Densities will be explained

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

ACPD

9, C10356–C10365, 2010

This will be mentioned

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

This is more common at higher temperatures, but organic polymers are an additional explanation. These will be mentioned in the paper.

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

Yes, both temperature and RH were changing at that time. The text will be reformulated so that these fluctuations are the most likely explanation.

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

An explanation and references to Eq. 2 and Tables 2 and 3 will be given

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

Reference to section 3.3 will be given.

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

ACPD

9, C10356–C10365, 2010

This figure would be unreadable in that case. Therefore, these will be shown in the supplementary material.

Technical Corrections:

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

"Hundreds" will be changed to "thousands"

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

The number 5 % will be removed

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

It will be said that there were 204306 inhabitants at the end of 2005

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

It will be mentioned that the equation is based on the ZSR equation

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

ACPD

9, C10356–C10365, 2010

Reference to Tiitta et al., (2009) will be added.

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

Will be corrected

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

Will be corrected

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

This will be removed

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

Will be corrected

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

This will be clarified

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

ACPD

9, C10356–C10365, 2010

Interactive Comment

It will be clarified that they are means. Medians (50th percentiles) will be shown in the supplementary material.

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

Units will be changed to g/cm^3

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

Current format is preferred, because half of the correlation matrix values would be duplicates and the data in the table can be ordered according to increasing correlation coefficients. In addition, both r and r^2 are commonly used in the literature.

P21888: Suggest thicker lines for clarity.

This figure will be extended to cover both columns in the ACP format, so the lines will be thicker as well.

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