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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterization of a large biogenic secondary organic aerosol event from eastern Canadian forests" *by* J. G. Slowik et al.

Anonymous Referee #3

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This paper reports measurements of elevated mass concentrations of organic aerosols at a Canadian site during northerly conditions. The authors provide a detailed analysis of the data and conclude that this is due to biogenic aerosol formation. Not only are biogenic aerosol concentrations reported that are much higher than those in previous studies, results from a regional model appear to broadly support the measurements. The paper is a thorough study and offers new insight and should be published in ACP providing the authors address several areas.

General Comments 1) The paper points out that the agreement between the elevated measured OA and the AURAM model results contrasts with the reported gross under-

prediction of measurements by models in polluted regions. However, what the paper doesn't discuss is that recent studies in tropical biogenic environments do show reasonable agreement between measurements and models (e.g. Chen et al., GRL, 2009), though not at such elevated concentrations as are reported here. It is also not discussed whether the model performs better in these environments or whether there are multiple compounding errors. Capes et al. (2009) show that whilst there is good agreement between measurements and a global model over the sub Saharan African region during the wet season, steady state calculations show that the measurements are considerably higher than would be expected from the precursors. They use different yields and atmospherically relevant precursor concentrations and show that there is a great variability in these parameters and may give a false impression of the goodness of the agreement between measurements and global models. The authors need to tackle this question in the paper for their environment I think.

2) There is new evidence (Kiendler-Scharr et al., 2009) that isoprene may inhibit SOA formation via terpenes by providing an OH scavenger. If this is an important mechanism then it will greatly reduce the SOA formed over tropical regions where isoprene emissions dominate those of terpenes, whereas in boreal regions, where terpene emissions dominate, one might expect a greater SOA formation. The results in this paper are consistent with this though the results from Hytialla are not. I am aware that the authors may not have been aware of the KS et al. results when preparing the ACPD paper but I would encourage them to include such a discussion and identify ways of testing this in future studies. I would also encourage a summary of current findings on field measurements in isoprene and monoterpene dominated environments and a discussion of the consistency and differences in the results.

3) The authors stress the finding that AURAMS agrees with the measurements during the biogenic event is a novel result. As noted above, this has been observed a few times previously. However it remains an important finding. However the model description shows that a considerable amount of new yield data has been used. The changes

that these yield data make to AURAMS output in a range of situations from those previously used by AURAMS and other models are not commented on or referenced, they need to be, this is important. Capes et al., (2009) show that such changes can be very large. Are the authors sure that the reason for the good agreement is because of the biogenic situation is different to the anthropogenic one or due to changes in yield data? Following up on this, I agree with an earlier reviewer that it would be very good to see how the simulation behaves compared to data in the polluted period.

4) The AURAMS modelling shows the agreement for the biogenic period, and then the agreement is not good for the last part of that period. What it does not show is whether AURAMS does or does not do a good job during the polluted period. The data appear to show that biogenics are also playing a significant role during this part of the experiment, do the model simulations bear this out? What can be learnt by showing where the measurements and model disagree as well as showing that they agree well?

5) The authors compare a 4 and 5 factor solution for the PMF analysis and conclude that as the third OOA factor retrieved from the 5 factor solution alters the OOA1 and OOA2 then it must be due to splitting and so reject the 5 factor solution. I am not sure that such a conclusion can be drawn at all. The mass spectrum of OOA3 in the supplementary material is indicative of a younger secondary organic aerosol – similar to those seen in laboratory chamber studies, whereas the OOA 2 in the 5 factor solution represents a higher 44/43 ratio and is indicative of a more processed OA. The time series shows that OOA3 is a relatively much larger contribution during the identified biogenic period than at other times – this at first sight is consistent with a closer source. PMF picks out factors which explain the variance, where one has multiple air masses demonstrating different ageing states of an organic aerosol during processing then different OOA can easily result. These are not splitting but may reflect different stages in the continuum of the ageing process. A boot strapping analysis should be performed on both the 4 and 5 factor solutions to see if the 5 factor solution is robust and a more rigorous discussion of why a four factor solution is used should be provided.

Specific points Abstract P 18114 line 1-2: Biogenic SOA was not measured in this study, OA was measured in this study and analysis is presented to show that this arises from biogenic sources.

Page 18114 line17: Radiative forcing as used by the IPCC refers to the radiative flux changes induced by man-made perturbations and not to natural systems. In this sense the SOA presented here is not a radiative forcing but represents a cooling on the Earth System via increased scattering of short wave radiation.

Page 18115 line 7-9: I do not understand this sentence – the authors seem to imply that not much work has been done studying SOA from biogenic environments because everyone was too busy studying polluted environments. This isn't really the case: there have been many studies in Hyttialla for a number of years in northern Boreal forests and studies in the Amazon Basin from several years ago. Furthermore, there has been considerable interest in studying biogenic OA systems in chambers for a number of years, more so perhaps than polluted environments.

Page 18115 Line 9: "significantly lower levels"...than those observed over polluted regions.

Page 18115 line 10: It would be useful to separate these studies into tropical, subtropical and northern boreal for the benefit of the reader and possibly give some insight into whether these are isoprene or terpene dominated locations.

Page 18117: Though the effect is only slight it would be useful to know whether the mass loadings presented are standardised to STP or whether they are based on the standard pressure at the time the AMS was calibrated?

Page 18117 lines 26-28: There is no need to define the collection efficiency twice.

Page 18119 lines 7: why isn't the period on the 24th and 25th when C3H3+ dominant and the K is low also classified as a biogenic period?

Page 18123 lines It isn't really necessary for this paper but the authors should comment

on the thermodynamics scheme used.

Page 18124 line 15: channel should be plural

Page 18126 lines 14-17: Though the correlation between HOA and NOx is good, there are a couple of periods when this is not the case. Are the authors able to determine what the cause of these differences might be? It appears that benzene is better correlated with HOA, yet the authors do not comment on this. Why might this be so?

Page 18126 line 20: The correlation with levoglucosan refers to previous studies, this should be made clear.

Page 18126 lines 20-24: I agree with previous reviewers, the correlations here are low and yet much is made of these correlations for determining the air masses. Some comment needs to be made and the justification be tightened up here.

Page 18128: It is good to see the new figure.

Page 18129: It would be good to provide dates on the identified periods.

Page 18129: The names given to the different periods in figure 5 are not mentioned earlier. They should be so that the link can be drectly established.

Page 18130 lines 7-9: Neither Yokelson et al or Reid et al measured the organic mass, rather they measured OC and converted to OM a neither used an AMS. Capes et al (2008) can be used also as they provide a direct measure of OM. However, both Capes et al and Yokelson et al are not from boreal forest fires and the OM/CO could be different, this needs to be commented on.

Page 18130 lines 22-24: The author claim that a tight correlation between OOA2 and CO means that the photochemical age of the air remains constant. I think what is meant is that the photochemical processing remains constant. I cannot see how a single point receptor receiving air travelling over a large areal extent of the boreal forest to the north can measure air parcels with a single photochemical age. Rather it is the footprint and

the photochemical environment across the region that is likely to remain constant.

Page 18130 lines 20-28: The authors discuss that no other sources can produce such high OOA2/CO ratios and therefore the source must be biogenic. I think a more detailed discussion is needed here to rule out other sources as the NOx is non-negligible and the CO is high (whilst the latter is consistent with a biogenic source it also means other sources cannot be rule doubt). How well is the CO explained by the available biogenic that has been oxidised? This section implies that the reason for the high OOA2/CO is because the SOA is biogenic in origin. A likely explanation for the high OOA2 is that close to source the available condensable material has a high concentration and even if it is reasonably volatile a significant amount will be present in the particle phase. This will evaporate on dilution further from the source field. The high OOA/CO are a feature of the proximity and strength of the source not that the source is biogenic per se. This needs to be discussed.

Page 18131 lines 11-16: It isn't clear to me how the 600 ppb increase is obtained from figure 5. The intercept during the biogenic period looks like it intercepts the x axis at around 120 ppb. How is the background derived to obtain the secondary contribution to this number?

Page 18133 It appears that the BVOC are dominated by monoterpenes. Is this correct? What is the MT/ISOP emission ratio? Does this demonstrate that the precursors are dominated by MTs?

Page 18134 point 2: I am unsure what is meant here. Do you mean that the OM/CO is significantly larger for the biogenic period compared with other periods in this study or than is reported in the literature?

Page 18135 line 6: Include the lifetime and references for acetonitrile and potassium.

Page 18135 line 7: See Capes et al. (2008) for BBOA to OOA1 conversion time.

Page 18135 point 2: This argument is circular in nature. The data are being used to

test the AURAMS prediction, yet AURAMS is being used as evidence to interpret the data. The argument needs to be re-developed here.

Page 18135 point 4: The data shown in figure 10c may not be as definitive as the authors state in the point. The back trajectories arriving at Egbert at 1800 on the 12th and 13th have come from a NE direction - close to the fire sources shown in figure 10a. However, figure 10a is for the period between 12th and 14th. What happens to the fires in the preceeding days? If these fires were present on the 10th then it is possible that long range transport of biomass burning air may influence Egbert. As previous studies (Capes et al 2008) the mass spectral fingerprint of BBOA looks like that of OOA after several days so this cannot be used to rule out biomass burning influence.

Page 18136 lines 21-22: Though lower temperatures tend to slow reaction rates and imply lower rates of photochemistry due to lower sun angle, they will favour partitioning – perhaps the authors should comment.

Page 13186 line 29: Radiative impact not radiative forcing.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 18113, 2009.