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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.

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Comment 1:

It is claimed that high T (and the resulting enhanced BVOC emissions) likely produced the observed biogenic SOA event that produced 15 to 20 ug per m3 of organic aerosol. It is also asserted that this process is likely a large source for aerosol over the whole region, even in more urban locations to the south (see Conclusions). However, during the duration of the study period (roughly 5/12 to 6/15) there were many periods of similar high T, yet throughout this whole period there was no other evidence for large biogenic SOA contributions at the measurement site. This seems odd if the process really is generally widespread and of sufficient range to significantly impact urban areas. Thus more than T is important. Is the argument that most of the biogenic SOA is occurring significantly to the north of the site, and it is only occasionally transported south? I think it would also be of interest to know if the model agrees with the observations and predicts less of a biogenic SOA influence at that site during the whole study (not just select number of days, as shown in Fig 7)?

Response

During the other high-temperature periods, the sampled air arrives from the south, having passed through the Toronto region. This prevents identification of a significant biogenic SOA influence because (1) biogenic VOC emissions are dominated by isoprene, rather than monoterpenes, decreasing the SOA yield; and (2) the Toronto outflow contains high concentrations of anthropogenic SOA.

With respect to model/measurement agreement, Fig. 9 has been expanded to include all model and measurement data from the end of model spin-up (end of 3 June) to the end of the measurement campaign (15 June). Unfortunately, the end of the campaign prevents us from accomodating the reviewer's request to extend the figure past this date, though we agree this would be interesting. However, a detailed comparison between AMS and AURAMS data from mid-June to mid-July 2007 at a site in southwestern Ontario is underway and will be the subject of a future paper.

Comment 2:

In the Abstract and Conclusions it is stated that a regional model approximately predicts the event timing and accurately predicts the aerosol loading. This is summarized in Fig 9. Given the very different shapes in the temporal profiles of the model prediction and observations (Fig 9), is it meaningful to claim that the model is doing a good job in predicting SOA mass? For example, peak SOA is observed slightly after midday on 6/13/2007 and peak predicted SOA occurs very early in the morning (looks like near sunrise) on 6/14/2007. (It would be interesting to see more of the temporal profile past 1200 am 6/15/2007 where model and observations appear to significantly diverge). Thus in essence, averaged over some significant time interval (say 24hrs) the magnitudes agree. All the diurnal properties or processes are then lost and maybe the agreement is just fortuitous. For example, in Fig 9, the OOA tends to have daily peaks from noon to late afternoon on 6/12, 6/13, and 6/14, as expected since SOA formation is strongly diurnal. The model shows none of this structure.

Response

It is likely that the ability of the model to capture the fine-scale meteorological structure (vertical diffusion, deposition, horizontal transport) plays a large role in the fine-scale temporal differences between the model and measurements. The Egbert site experienced an abrupt change in wind direction (north to south) late on the 13th (i.e. the end of the biogenic period). Because Egbert is on the edge of the high regional SOA (see Fig. 7), this meteorology strongly influences the measurement/model agreement. The model/measurement divergence at the end of the period is thus likely caused by the model prediction of the location of the edge of the biogenic-influenced area. Such fine-scale variation might also prevent the diurnal patterns from being accurately resolved. This is now noted in the text.

Comment 3:

Pg 18118 line 7, give uncertainty in Eb (0.6 plus/minus what)? I suspect there is some level of uncertainty in the SMPS measurement, converting an SMPS number distribution to volume, and then using measured composition to convert to mass. Also, does calculating the AMS average collection efficiency for one period really prove that the method was quantitative throughout the whole study for all the different aerosol chemical components? This is a critical question since the authors claim that the measured OOA agrees with the predicted SOA from monoterpenes. Some estimate of the measurement uncertainty should be given when these types of statements are made.

Response

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We now report Eb as 0.6 +/- 0.1. The periods to which the two Eb estimation methods were applied has also been clarified: (1) the optical scattering-based method was applied to all data beginning on 25 May (when the system became operational); (2) the SMPS-based method was applied to the entire study.

Comment 4:

Pg 18118 line 25, it is not clear how the difference in the upper size limits of SMPS and AMS are reconciled for the comparison.

Response

The revised explanation reads: “AMS distributions were converted from mass to volume for each 15 min interval by the relationship dva = dm*(rho_p/rho_0)*(1/χ), where dm is the SMPS-measured mobility diameter, rho_p and rho_0 are the particle and unit densities, respectively, and χ is the dynamic shape factor. For this conversion, we assumed spherical particles (i.e. χ = 1) and component densities of 1.77 g cm-3 for sulfate, 1.74 g cm-3 for nitrate, 1.527 g cm-3 for chloride, a weighted average of the sulfate and nitrate densities for ammonium, and 1.2 g cm-3 for organics. The AMS and SMPS volume distributions were compared below the SMPS large-size cutoff of dm = 400 nm.”

Comment 5:

A significant portion of this paper is devoted to AMS spectra interpretation by factor analysis. A problem with factor analysis is over interpretation – something that this analysis is in my view approaching. In order to provide some confidence in the analysis the factors are compared to various independent tracers, however, often the correlations are really very poor. Eg., Pg 18126 lines 15 and on, the correlations between F1 (HOA) and NOx, and F1 and Benzene are low (less than 50% of the variation can be explained), moreover, F2 (BBOA) correlations (r2) with K, levoglucosan (both inferred from AMS data), and independently measured acetonitrile, etc are very low (_

0.3) – any insights why? Is this typical? Based on this data, labeling these as anthropogenic or biomass burning seems questionable. This raises concern over how well PMF uniquely identifies the OOA-1 and OOA-2 parameters. I think it might be worth discussing if the main conclusions reached in this study are sensitive to the PMF analysis results. My impression is that they are not.

Response

For the anthropogenic traces, variability between these HOA, NOx, and benzene is expected to result from changes in emissions source profiles or relative contributions. For example, the relative intensities of these three species may vary depending on whether the site experiences a rapid transit from Toronto, slower transit from Toronto, or a mixture of Toronto air and highway emissions from the east/southeast. However, Fig. 2b indicates that while the relative intensities of these species change from plume to plume, the temporal correlation is good, providing confidence in the HOA apportionment.

In the case of biomass burning tracers, both potassium and acetonitrile are known to be problematic. The issues with the AMS potassium measurement (competing electron impact/surface ionization pathways, interference from C3H3+) are discussed in detail in the manuscript. For acetonitrile, recent high resolution PTR-MS measurements in downtown Toronto have indicated an interference at m/z 42 from the C2H2O+ ion [A. Vlasenko, personal communication, 2009]. This likely influences the acetonitrile time series during periods of Toronto outflow, e.g. the elevated acetonitrile periods between 25 May and 6 June. As a result, we do not expect more than a qualitative correlation between BBOA and these tracers. For identification of BBOA, we also note the characteristic fragments at m/z 60 and 73, the intensity of which is closely correlated throughout the study, and the overall similarity of the BBOA mass spectrum to levoglucosan and wood burning reference spectra.

Comment 6:

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Page 18128, lines 6-8. Can it really be stated that a large fraction of OOA-2 is formed within half a day give that: MVK+MACR to OOA-2 r2 is roughly 0.6 and the MVK+MACR vs OOA-1 (aged OA according to this paper) r2 is 0.2. I would characterize it as: some fraction, larger than that found in OOA-1, is possibly associated with freshly formed aerosol.

Response

For a correlation to be observed between OOA-2 and MACR+MVK, a large fraction of the OOA-2 mass must be produced before a large fraction of the MACR+MVK is destroyed. For comparison, note the lack of correlation between OOA-2 and monoterpenes, or the improved correlation of OOA-1 with long-lived acetone, rather than MACR+MVK. As the reviewer notes, the weak correlation of OOA-1 with MACR+MVK does suggest that some OOA-1 is also formed on this timescale; however the much-improved correlations of OOA-1 with longer lived species suggest this to be a lesser fraction. This is now stated in the manuscript.

We also note that the OOA-2/MACR+MVK correlation is better during individual periods than during the study as a whole (e.g. Rˆ2 = 0.71 during the biogenic period). (This is similarly true of the OOA-1/MACR+MVK correlation, which has Rˆ2 = 0.43 for the biogenic period.) This correlation is degraded when the study is considered as a whole because OOA-2 is also produced in the Toronto outflow, from different VOC precursors.

Comment 7:

Page 18129, lines 13, 14, What is the variability given for OOA-2 fractions (eg, 65 percent plus minus 10 percent). Is this the standard deviation?

Response

The reported uncertainties are the standard deviation of the OOA-2/organic mass fraction time series. This is now stated in the manuscript.

Comment 8:

Page 18133 lines 15 -20 and Fig 9. The authors do make convincing arguments that the predicted SOA from monoterpenes is in reasonable agreement with observations (ignoring for the moment that the timing of the event is off). But does that really prove that it is correct? I would use the word consistent. In my view this leads to overreaching arguments later in the paper regarding possible influence of biomass burning. The authors believe that because the predicted SOA is of similar magnitude as observed OOA that proves no biomass burning influence. Given the uncertainty in SOA yields, AMS measurement uncertainty, PMF analysis, etc this argument should be qualified.

Response

We agree with the reviewer's choice of words and have revised the sentence as follows: "This indicates that the high SOA concentrations during the biogenic event is consistent with oxidation primarily from monoterpenes."

The reviewer also discusses the implications of the agreement between predicted and measured SOA on with respect to a potential biomass burning influence. Here we also agree that this agreement is, by itself, insufficient to rule out biomass burning. However, we do not make this argument. Rather, the agreement of the measured and predicted SOA (which the model suggests is driven by monoterpene oxidation) is one of several pieces of evidence against significant biomass burning influences presented in section 3.3.3.

Comment 9:

Page 18136, line 4. Given the ranges in AOD shown in Fig 9, it could be argued that the AOD data do not show the large increase in SOA (one could almost draw a flat line through the AOD vs time data.

Response

While we acknowledge that the AOD levels in Fig. 9 do not approach those observed to the north of the site (see Fig. 10), the comparison of the data points and error bars at the beginning and peak of the biogenic period do indicate a statistically significant increase in AOD.

Comment 10:

Page 18136, Line 10; it takes some imagination to infer from this graph that areas to the north were also from biogenic SOA. Maybe the scale should be changed to focus more on the region of interest.

Response

The influence of biogenic SOA on AOD north of the site is inferred from the spatial similarity between the high AOD in Fig. 10a and the AURAMS SOA predictions in Fig. 7. This has been clarified in the text.

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