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Comment

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

J. G. Slowik et al.

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Comment 1:

Page 18122, line 27: I guess you mean SESQ emissions were a factor of 0.16 times the monoterpane emissions? The sentence is ambiguous as is.

Response

The reviewer is correct, and the sentence has been modified accordingly.

Comment 2:

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Page 18123, line 25: This is a different density than mentioned above for the conversion of mass loading into volume (page 18118, line 24). Why?

Response

The density used for the AMS/SMPS comparison is an estimate for the entire organic fraction, while the AURAMS density applies exclusively to SOA. For the AURAMS SOA density, we note that recent volatility basis set models have used 1.6 (Tsimpli et al., 2009) and 1.4 (Shrivastava et al., 2008). To avoid confusion, the AURAMS density is now referred to as an “SOA material density.”

While omitted from the paper to simplify the discussion, the AMS/SMPS comparison was also conducted with the organic density calculated based on the concentrations of the individual PMF factors, assuming 0.8 g cm⁻³ for HOA, 1.6 g cm⁻³ for BBOA (from levoglucosan), 1.5 g cm⁻³ for OOA-2, and 1.7 g cm⁻³ for OOA-1. This did not significantly alter the estimated collection efficiency.

Comment 3:

Page 18125, line: I suggest using “evaluated” instead of “validated”.

Response

We agree and have modified the manuscript.

Comment 4:

Page 18125, lines 5-13: I was confused about this. You mentioned that panel d has significantly less structure than panels a-c, so from the legend I would conclude that going from 4 to 5 factors still improves the quality of the PMF fit. However, the text mentions that 4 is the optimal number.

Response

Because the plotted quantity is the change in the time-dependent contribution to Q be-

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tween solutions (i.e. rather than the contribution itself) the reduced structure in panel d indicates that the 4 and 5 factor solutions are approximately equivalent in their ability to explain the data. That is, the Q-contribution time series for the 4 and 5-factor solutions are very similar. Considering the lack of improvement following from an increased number of factors, the absence of tracer data supporting a 5-factor solution over the 4-factor, and the known factor mixing/splitting artifacts observed in synthetic datasets at excessive number of factors [Ulbrich et al., 2009a], the 4-factor solution is considered optimal. This has been clarified in the text.

Comment 5:

Page 18127, line 6: Eliminate “with”.

Response

The paper has been modified.

Comment 6:

Page 18128, lines 11-13: I cannot see the dashed periods in Fig. 4.

Response

The shaded periods were mistakenly omitted from the initial manuscript. A revised version of Fig. 4 was uploaded to the online discussion and is contained in the manuscript.

Comment 7:

Page 18130: lines 8-11: deCarlo (ACP 2008) observed OA/CO ratios in biomass burning plumes that were much higher than mentioned here. I believe that the variability in biomass burning emissions is too high to rule out a biomass burning origin based on the OA/CO slope.

Response

We agree with the reviewer that the high $\delta_{\text{OM}}/\delta_{\text{CO}}$ ratio during the biogenic

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case study is not, by itself, conclusively indicate the absence of a biomass burning influence, and emphasize that this observation should be considered as one of a number of pieces of supporting evidence. Because of the large variations in previously reported delta_OM/delta_CO, we now compare the ratios from this study to previous measurements in a new table, Table 1. We include the DeCarlo et al. (2008) study cited by the reviewer, in which a maximum value of $\sim 80 \mu\text{g m}^{-3} \text{ ppm}^{-1}$ was observed in biomass burning-influenced urban outflow. As discussed below, we conclude that the biogenic case study delta_OM/delta_CO is higher than previous observations in fresh or aged biomass burning plumes, however due to variations in source emission ratios and atmospheric processing, the delta_OM/delta_CO alone does not completely rule out a biomass burning influence.

The new Table 1 compares previous measurements of delta_OM/delta_CO from fresh and aged biomass burning emissions to the biogenic, biomass burning, and urban outflow case studies (see Figs. 4 and 5a). To our knowledge, the highest delta_OM/delta_CO values reported for fresh emissions are on the order of $120 \mu\text{g m}^{-3} \text{ ppm}^{-1}$ [Yokelson et al., 2007a]. There are significant uncertainties in the effect of atmospheric processing on the delta_OM/delta_CO ratio. Capes et al. [2008] observed a constant $51 \mu\text{g m}^{-3} \text{ ppm}^{-1}$ value independent of airmass age. On the other hand, some studies indicate the $\delta\text{DOM}/\delta\text{CO}$ value may increase due to atmospheric processing (see Table 1). To our knowledge, the highest reported value is $200 \mu\text{g m}^{-3} \text{ ppm}^{-1}$, from laboratory aging of yellow pine (flaming with embers) [Grieshop et al., 2009]. Thus the previously reported delta_OM/delta_CO for both fresh and aged biomass burning emissions are lower than that observed during the biogenic case study ($234.4 \mu\text{g m}^{-3} \text{ ppm}^{-1}$). However, due to the large variations in source emissions profiles and atmospheric processing, we cannot rule out the possibility that aged biomass burning emissions could approach the measured ratio.

Reference: Grieshop, A.P., Logue, J.M., Donahue, N.M., and Robinson, A.L.: Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 1:

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Comment 8:

Page 18131, lines 13-16: Hudman et al. (GRL 2008) calculated secondary CO mixing ratios of 25 ppbv or higher. Hudman et al. used biogenic emissions from MEGAN, which are significantly higher in the eastern U.S. than the emissions according to BEIS used in AURAMS. I suspect that differences in emissions inventories may explain why earlier estimates of secondary CO gave lower mixing ratios (Granier et al., *Atmos. Environ.* 2000; Kanakidou and Crutzen, *Chemosphere* 1999). Some discussion of these uncertainties is warranted.

Response

We have revised the statement to note that the Hudman et al. study calculated secondary CO of at least 25 ppbv. Because (1) our purpose in comparing the Hudman et al. and Miller et al. (see Comment 9) studies is simply to note that the observed photochemical CO at Egbert is in agreement with previous predictions and (2) the intent of the paper is not to compare AURAMS CO predictions with other models, we feel a discussion of uncertainties in regional CO models would distract from the focus of the paper.

Comment 9:

Page 18131, lines 16-18: The paper by Miller et al. (ACP 2008) should be cited and discussed in this regard.

Response

We now note that the high levels of secondary CO in this study are consistent with the model/measurement comparison of Miller et al., which suggested a significant source of CO from biogenic VOCs for the continental United States during summer.

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Comment 10:

Page 18131, lines 19-22: Monoterpenes may be the dominant precursor of SOA in this region, but why are they assumed to be the dominant precursor of CO in this analysis? According to Hudman et al. (GRL 2008) and Granier et al. (Atmos. Environ. 2000), isoprene is a much more important precursor of CO than monoterpenes. Assuming that a significant fraction of the CO during the biogenic period came from isoprene oxidation, the analysis would have to explain a much higher SOA/CO ratio from monoterpenes than it currently does in order to be consistent with the measurements.

Response

The Hudman et al. study focused on the continental US, while Granier et al. looked at the global CO budget. For both these studies, biogenic VOC emissions are dominated by isoprene. However, the airmass discussed in this study originated from the Canadian boreal forest, where the monoterpene emissions are larger. A comment on the possible contribution of isoprene to CO and SOA levels has been added to the discussion of uncertainties in section 3.3.1.

Comment 11:

Page 18132, lines 8-9: A NOx level of 1 ppbv would actually point to non-negligible anthropogenic or biomass burning emissions, in contrast with the designation of these air masses. I suspect such mixing ratios may be close to the detection limit of the TECO instrument? Some discussion of this is needed in section 2.2.3.

Response

The reported NOx levels are increased by the smelter plume from Sudbury on June 11, which also increases sulfate, but does not significantly affect the organic concentration or composition. When this period is excluded, the mean NOx is 0.78 ± 0.41 , with a maximum value of 2.02 ppbv. These concentrations are slightly above the instrument detection limit (~ 0.2 ppbv). Because the Egbert site is located in a semirural rather

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than remote area, a small NOx background is expected. This is now stated in the manuscript.

Comment 12:

Page 18132, lines 10-14: I guess the $\delta(\text{CO})/\delta(\alpha\text{-pinene})$ ratio represents the CO formed divided by the α -pinene removed? I was expecting this ratio to indicate the instantaneous enhancements as a function of time, in which case I expected this ratio to go to infinity as α -pinene gets removed within hours.

Response

$\delta_{\text{CO}}/\delta_{\alpha\text{-pinene}}$ is formulated in terms of the reacted α -pinene. This has been clarified in the manuscript by changing the notation to $\delta_{\text{CO}}/\delta_{\alpha\text{-pinene reacted}}$.

Comment 13:

Page 18132, lines 15-24: Ng et al. (ACP 2007) determined yields for α -pinene in high-NOx and low-NOx conditions and this work should be cited here as well. It might also be useful to convert the NOx emission rate in Fig. 6 to NOx mixing ratios.

Response

We have added the Ng citation and changed the range of previously observed SOA mass yields from α -pinene to 3-45% to include for the Ng et al. low-NOx results. We have also added Fig. 6b, which shows the Fig. 6 data in terms of average NOx and α -pinene mixing ratios.

Comment 14:

Page 18134, lines 16-18: As argued above, I do not believe that this argument is very convincing: deCarlo et al. (ACP 2008) observed similarly high OA/CO ratios in biomass burning plumes.

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Response

This issue was addressed in response to Comment 7.

We agree with the reviewer that the high δ_{OM}/δ_{CO} ratio during the biogenic case study is not, by itself, conclusively indicate the absence of a biomass burning influence, and emphasize that this observation should be considered as one of a number of pieces of supporting evidence. That said, the observed δ_{OM}/δ_{CO} ratio is higher than those previously report for either fresh or aged biomass burning emissions.

Comment 15:

Page 18135, lines 19-26: I disagree with that argument. Capes et al. (ACP 2008) showed a tight correlation between OA and CO at various distances from the fire location. Photochemistry changed the particle composition measured by AMS, but did not enhance the OA mass loadings relative to CO.

Response

We thank the reviewer for raising this point. While it is true that the δ_{OM}/δ_{CO} observed by Capes et al. did not vary with distance from the fire, the observed value was also a factor of 4.6 smaller than that observed in the present study for the biogenic period. The new Table 1 shows that this is generally true of previously near-source emissions, which are at least a factor of 2 smaller than the Egbert biogenic δ_{OM}/δ_{CO} . For the biomass burning δ_{OM}/δ_{CO} to approach that of the biogenic period, it is required that the δ_{OM}/δ_{CO} increase with photochemical age. In such a case, the point made in the initial manuscript regarding the tight OM/CO correlation holds. This point has been clarified in the manuscript.

Comment 16:

Page 18136, lines 2-15: I am not convinced that the MODIS AOD in Figs. 9, 10a and 10b is unaffected by biomass burning. The authors argue in section 3.3.3 that the enhanced OA measured at the surface was not from biomass burning, and I do not

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disagree with that analysis. However, the aerosols that determine the AOD can also be in the free troposphere. The authors show the observed fire counts in Fig. 10a, but transport of biomass burning plumes over much larger distances is routinely observed. For example, Fig. 10b averages data from 2001 through 2006, which period includes 2004 when fires in Alaska very significantly affected eastern Canada and the U.S. in June and July (e.g. Pfister et al., GRL 2005; McMillan et al., JGR 2008). The authors must do much more to rule out that their analysis of AOD is not affected by biomass burning.

Response

We have added a new figure, Fig. 10d, to the manuscript, showing MODIS AOD for the boxed region of Fig. 10a, AERONET AOD at the Egbert site, and MODIS fire counts over the entire region of Fig. 10a for the period June 9 to June 16. Fire counts are negligible until June 14. However, at this point, the wind abruptly shifts from north to south and Egbert samples the Toronto urban outflow; the fire emissions never reach the site.

The contribution of the 2004 fires to the 2001-2006 average of AOD is now noted in the manuscript.

Comment 17:

Page 18136, lines 16-24: The seasonal variation in AOD peaks in June (Fig. 10b). Average temperatures must be higher in July and August, but the average AOD in August is almost half of what it is in June. Thus far, the authors have interpreted their observations solely in terms of the temperature dependence of biogenic emissions, but there must be other factors.

Response

This is a very good point. In Fig. 10b, the AOD peak occurs from May to July; these months are indistinguishable given the uncertainties. As the reviewer notes, the AOD

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in August is lower. It is uncertain whether this is caused by meteorological or biological factors (e.g., monoterpane emissions have been observed to decline rapidly in the early fall). The factors governing the late summer/early fall AOD decrease would be an interesting issue for future study.

Comment 18:

Page 18136, line 25 – Page 18137, line 17: The authors calculate the forcing due to biogenic SOA and the CO₂ formed from biogenic VOCs. This flux of CO₂ is likely inconsequential compared to any imbalance between carbon uptake and respiration. Also, this would not constitute a climate forcing since it is a natural source of aerosol and CO₂. I believe this is the weakest part of the manuscript and is also unnecessary.

Response

The calculation of relative climate impacts of the biogenic SOA have been removed from the manuscript. We now simply note that the SOA will produce significant regional cooling effect, while the CO₂ will produce a smaller warming effect.

Comment 19:

Figure 2: The labeling should be changed. The caption identifies the top four panels with mass spectra as panel a and the bottom four panels with time series as panel b. However, the four mass spectra are also labeled a through d.

Response

The mass spectra labels have been deleted.

Comment 20:

Figure 7: The caption mentions that SOA is plotted, but the color scale gives OC. Which is right? OA, of course, is typically a factor of 1.6–1.8 times OC.

Response

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The caption is correct; SOA is being plotted. (In AURAMS coding, OC25 is SOA and PC25 is POA.) For clarity, the color scale label has been changed to “SOA”.

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