

## ***Interactive comment on “Diurnally resolved particulate and VOC measurements at a rural site: indication of significant biogenic secondary organic aerosol formation” by S. J. Sjostedt et al.***

**S. J. Sjostedt et al.**

steve.sjostedt@ec.gc.ca

Received and published: 6 March 2011

This manuscript reports measurements of VOC concentrations and aerosol loading and composition at a rural site during the summer, with an emphasis on understanding the sources of secondary organic aerosol (SOA). From VOC measurements and inferred OH concentrations, the formation of SOA from various precursors is estimated using a new, simple approach. It is concluded that the observed aerosol is dominated by SOA from biogenic precursors rather than from anthropogenic ones, and that biogenically-derived SOA is generally well-represented in models. The dataset is excellent, the topic is of great importance to the community, and I agree with the authors

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



that the goal of developing simple approaches in order to estimate key SOA precursors is an important one. However, I have a number of concerns about the general approach used, which have important implications for the conclusions, and thus need to be addressed before this work can be published in ACP.

Response: We thank the reviewer for their constructive comments. The paper now more carefully addresses the appropriate yields to be used in the SOA calculations. Also, the conclusions are more carefully stated in light of the uncertainties associated with this simple approach for calculating SOA formation, in particular the potential for upwind SOA formation from short-lived, anthropogenic precursors especially during periods of urban outflow. However, we also stress that the focus on the paper is upon assessing the contributors to the local production rate of SOA at Harrow, not to total SOA across the entire region.

My biggest concern is the key assumption in the calculation (equation 1) that the local production rate of SOA is the same at all points upwind of the sampling site. As the authors discuss, this implies that VOC emissions/concentrations are the same everywhere. I agree with the authors (p. 27334, line 9) that the use of diurnal profiles somewhat reduce the errors associated with this approach, but such errors could still be large. Particularly confusing is that despite making this assumption, and defending it on the grounds that the area around the sampling site involves similar environs, the authors then continually refer to possible changes to concentrations that occur from upwind chemistry. For example, Eq 2 implies that concentrations of aromatics are higher closer to sources than they are at the sampling site. In other words, the use of Eq 2 seems to be in conflict with the assumption of uniform VOC concentrations. The argument that the constant concentrations of HOA and benzene imply no loss by chemistry or deposition is also based on the assumption of point-source rather than dispersed emissions. My worry here is that the assumption of constant upwind concentrations of VOCs might be a good one for biogenic VOCs, but a poor one for anthropogenic VOCs. The net result of this could be to greatly overestimate the importance of bio-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



genic SOA precursors relative to anthropogenic ones, since the anthropogenic ones might be largely reacted away before reaching the sampling site, whereas the biogenic VOCs could be replenished. On a related note, the significant loss of aromatic compounds in the morning (about 500 ppt total) should contribute to SOA, since it is largely due to reaction with OH (from the CO data, loss by dilution is relatively small). But it is not clear that this SOA formation is captured in the present modeling work – early-morning OH is presumably low, which would have the effect of underestimating SOA formation during the time when anthropogenic VOC concentrations were highest. Is this the case? (How does a simple  $\Delta\text{HC} \cdot Y / \text{CO}$  calculation compare to results from equation 1?) Thus the major conclusions of the paper – that the SOA is dominated by biogenics, and models handle biogenic SOA well - might be heavily biased by the specific approach used. Before this paper can be published, the authors need to investigate this possibility, and discuss it in much greater detail.

Response: This is a fair comment, i.e. that there may be anthropogenic SOA formation upwind of the observation site that our simple analysis does not account for when using data from just one site. We are calculating local production rates of SOA at Harrow, and a problem may arise when we compare these production rates to the observed increases of SOA that may be driven by upwind emissions different from those close to Harrow. While we raised this limitation in the original version of the manuscript, the issue is deservedly addressed in more detail in the revised version. In particular, we are in agreement with the reviewer that this comparison is likely to be more accurate for the biogenic SOA production rates than the corresponding aromatic SOA production rates because the biogenic precursor emissions are likely to be much more uniform throughout the region. We now state this more clearly in the revised manuscript.

We have specifically tried to assess the role of the aromatic precursors to the SOA formation observed at Harrow in the following ways:

1. We have done the calculation suggested by the reviewer of calculating the amount of SOA that will form from the aromatics based on the extent of diurnal loss of the

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

aromatic, taking into account the appropriate SOA yield. Indeed, this even simpler approach yields results that are similar to those calculated in the more complete manner presently used in the paper using reaction rates. This comparison is now presented in the paper. 2. During the Border Air Quality Study, aromatic mixing ratios were measured by canister sampling and GC analysis in both Windsor (part of the Windsor/Detroit metropolitan region) and at a rural site (Bear Creek) 50 km to the east/northeast of Windsor/Detroit. As expected, it is seen that the toluene and C8 aromatic values are higher in Windsor/Detroit than at Harrow by roughly a factor of 4.0 and 2.8, respectively. This places an upper limit on the amount that we are underestimating the importance of the aromatic precursor, but only during the few days of Detroit outflow. Indeed, BTEX concentrations were also measured at Bear Creek and they are roughly a factor of two times lower than the values at Harrow. 3. To determine the potential impact of high anthropogenic emissions on SOA calculations, we have now performed our full set of calculations by excluding the time period of Detroit outflow, and for only the Detroit outflow period. The results for the campaign period without Detroit outflow are very similar to those calculated for the full campaign, suggesting that while BTEX aromatics certainly play a more important role during the Detroit outflow time period, they have a considerably smaller role to play when averaged over the full campaign. Interestingly, the amount of SOA from biogenic precursors formed during the Detroit outflow period is calculated to be roughly the same as that calculated during the full campaign.

My second major concern involves the values of the SOA yields used, which are never actually given anywhere in the paper. The yield expressions need to be given in their own table, for comparison with other SOA models. Most importantly, how did the authors account for the well-known dependences on aerosol loading and temperature? If these were ignored, and yields were taken directly from chamber measurements (which tend to be run at extremely high loadings), then the model-measurement agreement may just be fortuitous, arising from a cancellation of errors. For example, the authors use Lee et al (JGR 111:D07302, 2006) for their SOA yield from terpene ozonolysis;

C14368

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



that experiment was carried out with an aerosol loading of  $>400 \text{ ug/m}^3$ , and so the yield measured (41%) was much higher (by a factor of 3-10) than it would be under atmospheric conditions. (See, for example, Fig. 4 of Shilling et al, ACP 8:2073, 2008.) If this same approach was taken for all yields used, then the calculated SOA is being artificially “inflated”, possibly by a large amount (up to an order of magnitude).

Response: This is also a good point. In the original manuscript we aimed for experimental consistency by taking SOA yields measured by just one research group. However, it is certainly true that the Lee et al. (2006) yield for terpene ozonolysis is on the upper range of yields measured for this process, most probably because of the high aerosol loading. And so it does indeed seem more appropriate to use yields from other groups that have worked with lower aerosol loadings. And so, motivated by this comment, we have changed the yields that we use in the calculations for the biogenic precursors, leaving the yields for the aromatics as in the original manuscript. Specific details of the yields used are included in the revised paper. The yields do take into account the time-dependent aerosol loading as measured by the AMS. Given the uncertainties involved in the temperature dependence of the yields, we use only room temperature yields: average temperature from 6 am to 6 pm throughout the campaign was very close to room temperature, 24 oC. The temperature dependence of the reaction rate constants is used throughout given the low uncertainties in these values. The relative importance of monoterpene ozonolysis does indeed become smaller with the new yields, as illustrated in the revised manuscript. However, the overall results that come from using the analysis approach in the paper – i.e. that biogenic SOA precursors are still dominant over aromatic precursors for the full campaign – remains unchanged.

Other comments:

- In Table 1, how were the “Observed” values determined? The text (p. 27336) implies this is over the 6am-6pm timescale, but the numbers given for both organic and sulfate do not seem to match up to the data in Fig. 8. The timescale used should be made

C14369

ACPD

10, C14365–C14374,  
2011

Interactive  
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



clear in both the text and the table caption.

Response: We agree, this was not clear in the original version paper of the paper. In particular, the approach we used was to take the one hour average of the aerosol mass, where the time intervals were centered at the absolute minimum and at the absolute maximum values observed in the diurnal plot. This is now stated in the revised manuscript.

- A considerable fraction of the paper is devoted to describing the different aerosol types (PMF factors) and campaign episodes. Based on this (and in particular the text on pp. 27332-33) I expected that the model-measurement comparison would be done for these individual time periods. But instead data from the whole campaign was lumped together (section 3.3). I would strongly suggest looking at these episodes individually; while I agree that it adds noise (p. 27333, lines 1-2), it would also provide a lot of insight, both in terms of validating the general approach taken and exploring key SOA precursors. For example, how much greater in importance are the aromatic precursors when polluted air is sampled? (If the authors choose not to go this route, than the discussion of different PMF factors and campaign episodes should be shortened considerably.)

Response: This is a good suggestion, also arising comments of the other reviewer. We now present results for: i) the full campaign, ii) only the Detroit outflow period, and iii) the full campaign without the Detroit outflow period. The aromatic precursors indeed become of greater relative importance to the SOA formation during the Detroit outflow period.

- I would recommend substantial changes to the figures provided. Throughout the paper, the figures do not closely line up with the important points of the work. Figs 2-7 are either raw data or diurnally-averaged data – it's not clear why both are necessary, and these could probably be condensed down to just a few key plots. Figures 10-11 are comparison of observations with results from a detailed air quality model – which is a

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



very minor part of the paper, with no description of the SOA module and little discussion of the comparison with measurements. To me, these figures are more of a distraction than anything - in my first cursory skim-through I assumed the predicted results from Figure 11 were from Eq. 1 - and really belong in a separate paper. On the other hand, some key results of the paper are not represented in any figures, and instead are found only in Table 1. A graphical description of the results would be extremely useful – something like calculated SOA formation from each precursor as a function of time of day. Additionally, the time-resolved OH concentrations are obviously very important to the calculation, but little information as to their actual values is given. A figure showing these values would be very helpful.

Response: We had originally prepared the figures that show the individual contributions of different precursors to the SOA formation but did not include them in the submitted manuscript largely for length reasons. However, they are now included in the revised manuscript. We would like, however, to leave the other figures in the paper. In particular, the time series are necessary to delineate the different air masses studied, and the diurnal profiles illustrate the photochemical processes involved. We consider the figures comparing the AURAMS output valuable because they illustrate the accuracy by which a state-of-the-art chemical transport model can simulate SOA formation during the day, and quick comparison can be made to the similar ability of our simple model.

- An assumption implicit in Equation 1 is that SOA formation is instantaneous (arising from the single-step oxidation of a VOC). We know this is not always the case – SOA formation from isoprene involves at least two oxidation steps, so could occur over several hours – and this needs to be stated explicitly. This assumption is actually made in most current models, and is rarely articulated, but it's an extremely important caveat in studies that look at SOA formation over just a few hours (as opposed to a few days).

Response: This point is now made in the revised manuscript.

- For the reasons given above, I disagree with the assertions (p. 27338, lines 27-28 and

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

p. 27341, lines 6-7) that the sulfate comparison gives a rough idea of the uncertainties inherent in the estimate of SOA formation. Sulfate is formed from gas-phase chemistry in a single rate-limiting step ( $\text{SO}_2 + \text{OH}$ ), with a fixed yield (about 100%); SOA formation can occur of multiple oxidation steps, in yields that are complex, variable, and uncertain. Given this, I would thus argue that the uncertainties in the sulfate calculation (a factor of 2-3) are the LOWER limits to the uncertainties associated with SOA formation.

Response: It is now stated that the sulfate comparison is a rough measure of the accuracy of the OH concentrations and the CO normalization/diurnal analysis procedure only, but it does not include uncertainties that are special to the organic case, especially yields that are highly variable.

Minor comments: - P. 27323, lines 18-20. As written, the sentence is somewhat tautological; an OVOC is necessarily volatile, so it can't be of sufficiently low vapor pressure to condense.

Response: Wording has been changed.

- P. 27323, lines 22-25: Ng et al 2007 (ACP 7:5159, 2007) found the opposite NO<sub>x</sub> dependence for larger species.

Response: Wording has been changed.

- P. 27326, lines 26-28: part of this definition is that the evaporation has to occur on the timescale of about 1 second (the open-closed timescale of the AMS beamblock).

Response: This point has been added to the text.

- P. 27327, lines 25-27: without more evidence, it seems highly speculative to attribute Factor 4 to uptake of VOCs onto sulfate. Was this aerosol highly acidic?

Response: We agree, as now stated in the paper, this is speculative - the factor may be due to the reactive uptake of isoprene onto preexisting sulfate aerosol and/or condensation of early-generation isoprene reaction products. We cannot dis-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

tinguish between the two possibilities. Additional information concerning this factor can be found in Slowik et al., ACPD, 10, 24993–25031, 2010, and in its interactive discussion. In particular, look at Comments #3 and #8, and their corresponding Responses: <http://www.atmos-chem-phys-discuss.net/10/C13202/2011/acpd-10-C13202-2011.pdf>. Also, refer to Robinson et al., 2011, ACP 11:1039-1050.

- P. 27331, lines 6-8: Given that Factor 4 has a very low oxygen content (p. 27327, lines 21-23), I would not call it “oxygenated”. (Technically it is, but in AMS lingo, stuff usually isn’t considered oxygenated until it has an O/C ratio of 0.3 or so.)

Response: We have removed this wording.

- P. 27333, line 17: is “section 4i” a typo?

Response: This typo has been corrected.

- P. 27337, line 19: how is this distance (70 km) calculated? 12 hours at 3.3 m/s is 140 km; and to me an “extent” implies a diameter rather than a radius, so I would have said 280 km.

Response: We should have been more explicit. This is a rough calculation made for the period over which the majority of the SOA formation occurs, which we put at 6 hours. We have reworded this section.

- Table 1: “anthropogenic” should be replaced with “aromatic”. (Or, the same caveat on p. 27337, lines 9-13, should be included in the table header for clarity.)

Response: We have changed “anthropogenic” to “aromatic”

- Figs 7-9: the y-axis label should have the denominator in brackets (to emphasize the background correction is to CO, not to the whole ratio). Also, in Fig. 8d, the background CO is listed as 60 rather than 80 ppb. Is this a typo?

Response: We have made these changes, and, yes, 60 ppb was a typo.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Interactive  
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper