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Atmospheric
Chemistry
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Discussions

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.

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General comments

This paper presents an interesting analysis of a substantial dataset of aerosol and gas-phase properties measured in a rural region near the U.S.-Canada border. The manuscript is well written and informative. The subject matter–the contribution of biogenic VOCs to organic aerosol formation– is one that is relevant to climate forcing and atmospheric chemistry, and is of interest to a broad spectrum of ACP readers. The authors have made important contributions to this field in the past, and they place the results within the context of the extant literature.

Although there are many positive aspects to this Discussion, there are some issues that are troubling. The authors are making a quantitative argument with an analysis that is subject to several large uncertainties. While they recognize and discuss some of these uncertainties, they do not discuss at least one–mixing with the residual PBL layer–and they draw very strong conclusions given the potential difficult-to-quantify uncertainties.

The material in this Discussion certainly warrants publication in ACP, but revision of the manuscript is needed to address some of these issues and to perhaps tone down the conclusions.

Response: We appreciate this insightful review. Given the comments, we have adjusted the conclusions especially as they relate to potential uncertainties associated with this simple approach.

Specific comments

There are four major issues with the manuscript: 1) I am concerned with the role of mixing of the growing daytime PBL in this analysis. Examining Fig. 8, we see in the upper left frame (should be labeled "A") that the absolute concentration of fine aerosol organic mass is relatively invariant throughout the average diurnal cycle. There is an increase of about 2 ug/m3 in the early afternoon; otherwise the concentrations are 6 ug m-3 on average. The CO-normalized diurnal cycle (Fig. 8b) shows a 40% variation in OA/(CO-80ppbv), which is driven almost entirely by the afternoon decrease in CO (Fig. 6a) from _220 ppbv to _150 ppbv as the PBL ventilates. The assumption is that, if there is no SOA formation, the measured OA should decrease linearly with CO during the afternoon venting. The lack of such a decrease is analyzed quantitatively to determine SOA formation from measured precursor VOCs. However, there is no information available on the relationship between OA and CO in the tropospheric air that is being entrained into the growing daytime PBL. The implicit assumption is that OA and CO must scale linearly in this entrained air. But there are many cases where the air above the nighttime boundary layer is a residue from the previous day's PBL.

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Even more complex structures, including nocturnal jets, are frequent occurrences in central North America; these jets can transport pollution hundreds of km overnight. Complex vertical structures are common at night (Brown et al. 2007), and can have varying CO-aerosol relationships that potentially complicate the analysis. Because the CO-OA relationship aloft is not known, the authors should be very cautious about over-interpreting the results without characterizing and evaluating this additional uncertainty. A similar analytical approach was used during the MILAGRO campaign to evaluate SOA formation in the Mexico City area (de Gouw et al, 2009). The BAQS-Met case presented here is quite different from Milagro, where huge emissions from a megacity were topographically constrained and overwhelmed any possible contribution from the well-ventilated free troposphere aloft. In BAQS-Met, there is a large background of regional pollution (CO _200 ppbv!, OA_6 ug/m3), no topographical constraints to pollutant transport, and a complex mix of sources from biogenic to urban to regional to point sources. The increased complexity of the BAQS-Met case requires commensurate caution in interpreting the data. The authors appear to be aware of this complexity in terms of horizontal variability, but do not seem to have considered vertical variability and its effect on the derived SOA formation.

Response: This is an excellent point that is discussed in the revised manuscript. In particular, with this approach we are implicitly assuming that during boundary layer dilution the CO and OA of the diluting air scale with each other. While this may be true, it is not necessarily the case for all times during the study. However, as the reviewer points out, it is difficult to accurately quantitatively assess this effect. To give a sense for how strongly we may be biasing our results by using CO to account for dilution, we now present in the paper calculations performed where we do not normalize to CO. When we do this, the conclusion that biogenic precursors are significant does not change and the degree of SOA closure actually improves. As a result of this and other comments raised by the reviewers, we have reworded the conclusions made in the paper, in particular with respect to the uncertainties in the absolute amount of SOA formation that is occurring. We re-iterate what was stated in the original manuscript, i.e.

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a full chemical transport model that can follow such dynamical effects is the preferred method for absolute estimates of SOA formation across a region.

2) The authors argue (p. 27329, line 24) that, by averaging data to a diurnal profile, the uncertainties due to short-term fluctuations from specific sources are reduced. I would like to see a sensitivity study of the effect of averaging subsets of the data on the diurnal profile. If 50% of the data are excluded, are the results the same? 80%? 90%? There should be some way to quantitatively evaluate the impact of episodic events averaged into the diurnal profile on the analysis. A hint of the sensitivity is given on p. 27337, line 27, where using median values (rather than mean) results in a factor-of-two change in the SOA closure. This is an evident sensitivity that warrants further investigation.

Response: Yes, the reason that we performed the mean-to-median comparison was to gain a sense of the sensitivity to short-term fluctuations. To further address this issue, we have now performed the analysis by excluding the time period with the direct outflow from Detroit/Windsor. We do this in an attempt to assess the degree to which high anthropogenic conditions during these few days affected the overall conclusions from the study.

3) Equation 1 describes the production of SOA from lab-measured yields, first-order reaction rate constants, and the diurnal profiles of VOCs and OH. However, the yield Y is a result of absorptive partitioning and thus should be a function of the OA concentration. Since OA varies as a function of time, this means that Y should be within the integral, rather than a constant outside of it. Given the relatively low OA concentrations, Y will be considerably less than the maximal value that *may* have been used in this analysis.

Response: Equation 1 was incorrectly written in the manuscript, and the yield and rate constant should have been within the integral sign. Thank you for catching this. However, we did indeed calculate yields in a time (i.e. OA mass) dependent manner when the parameters for a two-product model were included in the literature cited, or else we used average values from those experiments. However, in response to a comment from the other reviewer, we have revisited the specific yields used in the calculations, especially for the biogenic precursors, taking into account OA mass dependence when appropriate. The details on the yields are in the revised version of the paper. We use room temperature yields given that the temperature dependence of the yields is uncertain and the average temperature from 6 am to 6 pm during the campaign was 24oC. However, we do account for the temperature dependence in the rate constant for loss of the precursor, given that those temperature dependencies are known well.

4) The results, as encapsulated in the abstract in conclusion, strongly state that the BAQS-Met region is ". . . a highly biogenically dominated region for SOA formation." Given the large regional background of _200 ppbv of CO and _6 ug m-3 of OA, I submit that upstream urban emissions followed by rapid (<1 day) SOA formation from semivolatile and intermediate-volatility compounds are also likely to be large contributors to the overall budget. The perturbation of the evident biogenic SOA formation, while quite important and interesting, needs to be placed in the context of the total OA budget in this region.

Response: The conclusions have been adjusted, and the potential for formation of SOA from unmeasured, short-lived urban emissions, especially during the Detroit outflow period, is re-stated. While such non-aromatic emissions were not measured, BTEX compounds were measured in Windsor (part of the Detroit/Windsor metropolitan region) during BAQS using canister sampling and GC analysis. Values at Windsor are higher than those at Harrow (factors of 4.0 and 2.8 times higher for toluene and the C8 aromatics, respectively), to give a sense of the representativeness of the Harrow measurements. BTEX was also measured at a rural site, Bear Creek, 50 km to the east/northeast of Detroit during BAQS. The Bear Creek values are lower than those at Harrow by about a factor of two, so the Harrow data may be leading to an overestimate of the aromatic contributions during times of non-direct Detroit outflow. We find that when the Detroit outflow period is removed from the analysis, the overall conclusions that the biogenic precursors dominate over the aromatic precursors remains valid, for the local production rate of SOA at Harrow. Note that we are not attempting to assess the overall SOA production rate across the whole region.

More minor comments: 5) The time-plots (Figs. 2-4) have different time axes (ticks, spacing, etc.) making it difficult to compare them. It would be helpful to add mirrored axes on the right to make it easier to read points off of the lines using a straight edge. Bars indicating the subsets of data used for later analysis (Detroit, southwestern flow, biogenic) would be welcome.

Response: These changes have been made.

6) In Fig. 7, MACR + MVK, which should be products of isoprene oxidation, do not appear to lag isoprene. Furthermore, a peak in these compounds at 11AM-noon matches SO2 in Fig. 6, which is attributed to mixing of SO2 from aloft. This is troubling for the closed, ventilated PBL system that is modeled.

Response: Yes, this may be due to some mixing down of isoprene oxidation products from aloft, and is thus related to the reviewer's first point. We now point out this observation in the revised manuscript.

Technical corrections a) "de Gouw" is sometimes shown as "De Gouw"

Response: Corrected

b) page 27326, line 11, "Detroit" should first be "Detroit, Michigan, USA"

Response: This change has been made.

c) p. 27325, line 19, place "(Fig. 1)." after ". . .Harrow"

Response: This change has been made.

d) p. 27325, line 20 "southwestern" not capitalized here; it was earlier.

Response: The text is now consistent.

e) p. 27326, line 25, was this a compact time-of-flight mass spectrometer?

Response: Yes, this was stated in the parentheses in this line.

f) p. 27329, line 20, what is meant by a 21-point running average? What is the time resolution of the data to which this smoothing is applied?

Response: The time resolution of the data is 5 minutes, as stated in the revised paper. A 21-point running average is calculated using the average of 10 points before and 10 points after each time point.

g) throughout manuscript, does "average" mean "arithmetic mean"?

Response: Yes, “average” means “arithmetic mean”. We now state this in the paper.

h) p. 27334, line 17, there is no "Sect. 4i".

Response. Thanks. This was a typo occurring at the time of ACPD publication, and should have read “Section 3.1”.

i) p. 27336, line 15, I believe you should reference an equation as "Eqn. 1".

Response: We have made this change.

j) p. 27337, line 28, "predicted" is misspelled

Response: Corrected

k) p. 27340, line 19, replace "fresh" with "modern"

Response: Done

l) p. 27346, line 20, should be Slowik et al., 2010a.

Response: Done

m) p. 28346, line 25, should be Slowik et al., 2010b

Response: Done

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n) p. 27346, line 31, remove capitalization of paper title

Response: Done

o) All figures, please use "A", "B" etc. to identify graph elements

Response: Done

p) p. 27354, Fig. 6, label for acetone/CO-80 line is odd

Response: Corrected

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 27321, 2010.