

## ***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.***

**Anonymous Referee #2**

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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

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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.

### 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  $\mu\text{g}/\text{m}^3$  in the early afternoon; otherwise the concentrations are  $\sim 6 \mu\text{g m}^{-3}$  on average. The CO-normalized diurnal cycle (Fig. 8b) shows a 40% variation in  $\text{OA}/(\text{CO}-80\text{ppbv})$ , which is driven almost entirely by the afternoon decrease in CO (Fig. 6a) from  $\sim 220$  ppbv to  $\sim 150$  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. 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

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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/m<sup>3</sup>), 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.

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.

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.

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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<sup>-3</sup> of OA, I submit that upstream urban emissions followed by rapid (<1 day) SOA formation from semi-volatile 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.

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.

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 SO<sub>2</sub> in Fig. 6, which is attributed to mixing of SO<sub>2</sub> from aloft. This is troubling for the closed, ventilated PBL system that is modeled.

Technical corrections

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

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

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

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

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

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?

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- g) throughout manuscript, does "average" mean "arithmetic mean"?
- h) p. 27334, line 17, there is no "Sect. 4i".
- i) p. 27336, line 15, I believe you should reference an equation as "Eqn. 1".
- j) p. 27337, line 28, "predicted" is misspelled
- k) p. 27340, line 19, replace "fresh" with "modern"
- l) p. 27346, line 20, should be Slowik et al., 2010a.
- m) p. 28346, line 25, should be Slowik et al., 2010b
- n) p. 27346, line 31, remove capitalization of paper title
- o) All figures, please use "A", "B" etc. to identify graph elements
- p) p. 27354, Fig. 6, label for acetone/CO-80 line is odd

References:

Brown, S. S., et al. (2007), Vertical profiles in NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> measured from an aircraft: Results from the NOAA P-3 and surface platforms during the New England Air Quality Study 2004, *J. Geophys. Res.*, 112, D22304, doi:10.1029/2007JD008883.

de Gouw, J. A., et al., (2009), Emission and chemistry of organic carbon in the gas and aerosol phase at a sub-urban site near Mexico City in March 2006 during the MILAGRO study, *Atmos. Chem. Phys.*, 9, 3425–3442, doi:10.5194/acp-9-3425-2009.

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