

## ***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 #1**

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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 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.

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 biogenic 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.

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; 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).

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 clear in both the text and the table caption.

- 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

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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.)

- 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 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.

- 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).

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

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.

- P. 27323, lines 22-25: Ng et al 2007 (ACP 7:5159, 2007) found the opposite  $\text{NO}_x$ -dependence for larger species.

- 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).

- 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?

- 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.)

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

- 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.

- 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.)

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- 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?

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