

## ***Interactive comment on “Secondary Organic Aerosol (SOA) yields from NO<sub>3</sub> radical + isoprene based on nighttime aircraft power plant plume transects” by Juliane L. Fry et al.***

### **Anonymous Referee #2**

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#### Summary:

The manuscript by Fry et al. addresses, for the first time, the potential to measure in-situ secondary organic aerosol (SOA) yields from isoprene oxidation in a power plant plume by aircraft. This is a completely original and timely study that aims to assess SOA yields in the ambient environment without the competing effects of wall loss, which has hampered most laboratory (reaction chamber) studies in the past. In this view, the paper is highly suitable for Atmospheric Chemistry and Physics. The authors determine isoprene-derived SOA yields from NO<sub>3</sub> oxidation in the plume based on measured enhancements in aerosol organic nitrate and isoprene loss in the plume

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relative to aerosol organic nitrate and isoprene concentrations outside of the plume. The authors find that isoprene-derived molar SOA yields from reaction with NO<sub>3</sub> is on the order of 9%, and mass-based SOA yields are 27%, larger than those measured previously in the laboratory (12-14%). The authors conclude that the relatively larger SOA mass yield is due to the longer plume age and processing (forming more nitrates) compared to apparently shorter processing time in chamber studies. While I thought the paper was creative, well written, and well supported by the literature, before I can fully support publication, I encourage the authors to address my points of concern in a revised manuscript as stated below.

#### Major comments:

1. Although I thought the authors did their due diligence by addressing several of the caveats in this study, I have a couple of additional concerns (but possible solutions) with the calculation of SOA yield that I encourage the authors to address in a revised manuscript.

First, the authors use isoprene measured outside of the plume as the initial (starting) concentration and from that derive the SOA yield based on the difference in isoprene concentrations measured inside and outside of the plume. Ideally, I think you would want to use isoprene measured from the point of plume emission as the starting concentration of isoprene, i.e., measure the isoprene concentration in the plume near the point source, and then measure isoprene in the plume at a distance further downwind of the point source, because then you know how much of the initial isoprene in the plume (same air mass) was consumed. My main concern with using isoprene outside of the plume as the starting concentration is that it does not necessarily represent the isoprene that has undergone processing in the plume. According to the isoprene time series shown in Fig. 2, in the span of 5 minutes, isoprene outside of the plume can be 700 ppt, 500 ppt, and 300 ppt, for example. Thus, the SOA yields reported in this work depend critically on the choice of concentration measured outside of the plume. While I am not suggesting the authors are wrong in their approach, it might be helpful

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if the authors could identify a case where they sampled the same plume twice at different locations downwind of the point source and calculate the SOA yield based on the difference in isoprene/nitrate measured in the first transect and a later transect. This would at least strengthen/validate the approach. Alternatively, it may help to show that “background” isoprene measured outside of the plume does not vary significantly near and further downwind of the plume source.

Second, what is the impact of O<sub>3</sub> (and other oxidants) on isoprene loss in the plume? I thought there would be more discussion of this – while the reaction rate of O<sub>3</sub> with isoprene is several orders of magnitude less than NO<sub>3</sub>, the concentration of O<sub>3</sub> can be several orders of magnitude greater than NO<sub>3</sub>, and therefore may rival NO<sub>3</sub> in regards to isoprene consumption in the plume at night. In the Edwards, et al. [2017] study referenced by the authors, O<sub>3</sub> accounts for 45% of the BVOC consumption at night. In this study, the SOA yield is based on the premise that VOC consumption is controlled entirely by NO<sub>3</sub>. If other reactants that consume isoprene (e.g., O<sub>3</sub> and OH) are present in sufficient quantities, the calculated yields might overestimate the contribution from NO<sub>3</sub>. I encourage the authors to address this more explicitly, e.g., by calculating the relative loss rates of isoprene at night by NO<sub>3</sub>, O<sub>3</sub>, and OH.

2. The scatter and limited number of observations used to calculate the average yield as shown in Fig. 5 may be a point of concern. Uncertainty bars on the data would certainly help to convey how far off from the fit the measurements truly are. Often, SOA mass yields are expressed as a function of the change in particle mass ( $\Delta M$ ); if the authors were to instead plot plume change in pRONO<sub>2</sub> mass as a function of plume change in isoprene mass, could it be that the larger/smaller enhancements in aerosol organic nitrate mass simply result from a shift in equilibrium partitioning more/less to the particle phase owing to a larger/smaller  $\Delta M$ ? I encourage the authors to show the effects of  $\Delta M$  in some capacity, e.g., by normalizing each point in Fig. 5 by the measured  $\Delta M$  (i.e., difference in  $M$  between inside and outside of plume) and/or making a separate figure to show mass yield as a function of  $\Delta M$ . Alternatively, instead of using

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$\sqrt{n}$  as the bubble size in Fig. 5, scale bubble size by  $\Delta M$ .

#### Minor comments

1. In the SOA molar yield calculation, the authors first convert the aerosol nitrate from mass concentration units to equivalent ppt assuming the aerosol organic nitrate has a molar mass of 62 g mol<sup>-1</sup>. This seems far too small a molar mass expected for isoprene+NO<sub>3</sub> oxidation products. Why not assume a molar mass consistent with the first generation carbonyl nitrate produced from isoprene+NO<sub>3</sub> (MW=145 g mol<sup>-1</sup>) (Jenkin et al., 2015) or another suitable organic compound as done later with the SOA mass yield calculation?

2. Page 2, line 52: “review”

3. Page 3, lines 92-94: Please include reference.

4. Page 9, Eq. 1 (lines 367-371): Equation (1) has  $k_1$ , whereas text states  $k_2$ .

5. Page 14, lines 500-502: It’s probably more correct to write the production rate of isoprene oxidation products by NO<sub>3</sub> reaction is greater than for monoterpenes.

6. Figure 5: It would be helpful to the readers if in the legend, the symbol for  $\Delta p\text{RONO}_2$  were black with a color scale next to the current legend (the red color of the symbol is confusing with some of the points being red). A separate legend for marker/bubble size would also be helpful.

#### References

Edwards PM, et al. (2017) Transition from high- to low-NO<sub>x</sub> control of night-time oxidation in the southeastern US. *Nature Geoscience* 10(7):490-+.

Jenkin ME, Young JC, & Rickard AR (2015) The MCM v3.3.1 degradation scheme for isoprene. *Atmos. Chem. Phys.* 15:11433-11459.

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