

This is an interesting study on the topic of the comparability of SOA studies performed in large environmental chamber studies and fast portable oxidation flow reactors (OFR). OFRs are gaining increased use in recent years in the atmospheric chemistry community. We commend the authors on their work in conducting flow reactor experiments and compiling these comparisons of chamber and flow reactor SOA formation studies, and hope that they and others will continue to explore these topics in the future.

However, there are some key aspects related to documentation of conditions, applications of experimental methods, data presentation, and data interpretations that are not well described in the paper. In our opinion these should be addressed before publication of this manuscript.

### 1. OH exposure:

As Referee 3 noted, the experimental section is lacking some key details. One critical aspect, in particular, is the lack of information on how the OH exposure ( $\text{OH}_{\text{exp}}$ ) is calculated. The only reference to  $\text{OH}_{\text{exp}}$  calculations appears in Sect. 2.1 (p 30581, lines 8-13) as “OH concentrations were varied by changing the UV light intensity, and were quantified by measuring the decay of  $\text{SO}_2$  and applying the known  $\text{OH}+\text{SO}_2$  rate constant (Davis et al., 1979).” Depending on the details of how such experiments were done, there could be substantial errors in the estimated  $\text{OH}_{\text{exp}}$ . However there is not sufficient detail in the manuscript to ascertain whether this is the case or not. It would be very useful to the community and the future users of the results of this paper if more details were provided, so readers and other researchers don't have to speculate whether disagreements may be due to errors or uncertainties in  $\text{OH}_{\text{exp}}$ .

As discussed in Ortega et al. (2013) and Li et al. (2015), high VOC concentrations (or high concentrations of other compounds that react with OH) can “suppress” OH by shifting OH to  $\text{HO}_2$  in the reactor, resulting in much lower OH exposures than measured for the same conditions in the absence of added “external OH reactivity” ( $\text{OHR}_{\text{ext}}$ ). Measurements and modeling carried out by our group (using reactors that employ either 254 nm only or both 254 + 185 nm wavelengths from mercury lamps to generate OH) suggests this “OH suppression” can reach 1-2 orders-of-magnitude for high  $\text{OHR}_{\text{ext}}$  (100-1000  $\text{s}^{-1}$ ). Very high  $\text{OHR}_{\text{ext}}$  were indeed used in the experiments described in this paper.

With the information provided, it is impossible to know if the effects of OH suppression from high  $\text{OHR}_{\text{ext}}$  were accounted for or not in this study. Several critical pieces of information include:

- Were the  $\text{SO}_2$  decay measurements performed only “offline”, i.e. in the absence of VOC? Or were they carried out “online” (in the presence of added VOC)?
- If offline, at what range of  $\text{OHR}_{\text{ext}}$  (i.e.  $\text{SO}_2$  concentrations)?
- What  $\text{H}_2\text{O}$  concentrations were used for the calibrations and how do they compare to those used in the VOC experiments, if those were different experiments?
- What input  $\text{O}_3$  levels were used for the  $\text{SO}_2$  and VOC experiments?

- Were the calibrations and SOA experiments conducted close in time? Hg lamps age with time and the same light power setting may not correspond to the same UV flux if multiple months have passed.

H<sub>2</sub>O and O<sub>3</sub> concentrations will strongly affect both OH<sub>exp</sub> and degree of OH suppression for a given lamp setting. If calibrations were not conducted at relevant conditions or characterization of the effects of OH suppression estimated, a discussion of possible biases should be included in the manuscript, or (better) OH<sub>exp</sub> calibration experiments should be conducted under conditions representative of the OHR<sub>ext</sub> of the experiments. If differences in OH suppression between calibrations and VOC experiments were corrected for, the details of such corrections should be thoroughly described in the paper.

Also, for conditions with high VOC concentrations, RO<sub>2</sub>+SO<sub>2</sub> reactions may cause substantial decay in SO<sub>2</sub>, not attributable to OH (Kan et al., 1981; Richards-Henderson et al., 2014). Therefore, if online calibrations were conducted (i.e. if the SO<sub>2</sub> was introduced at the same time as the VOC) this may cause a substantial overestimate in OH<sub>exp</sub>. If additional high OHR<sub>ext</sub> calibrations/characterizations experiments are conducted, use of an additional compound that reacts with OH but not RO<sub>2</sub>, such as CO, would help eliminate errors arising from that cause.

## 2. Interpretation of SOA yield comparisons:

This concern about uncertainties in the quantitative OH exposure relates to Referee 2's comment about the authors' interpretation of Fig 5 that "It is not evident to me from Figure 5 that SOA yields at comparable OH exposures are a factor of 2 to 10 lower in the flow reactor than in chambers." For Fig 5a and Fig 5b, it appears that a decrease in OH exposure on order of a factor of ~2 would make the yields between the chamber and PAM indistinguishable for overlapping OH<sub>exp</sub>. Therefore, unless the authors can demonstrate that the uncertainty in OH<sub>exp</sub> exposure is substantially less than a factor 2 with their methods, this statement should be removed from the paper (especially from the abstract and conclusions, where it appears in less quantitative terms), or possibly modified to reflect only the factor of 2-3 difference for isoprene SOA under the experimental conditions of these studies (and also probably the experimental agreement for the other compounds). Such low uncertainty of only a factor of 2 in OH<sub>exp</sub> is difficult to achieve in practice with a PAM in our experience, and in any case requires careful work on this topic, something that cannot be assessed from the current version of the paper.

Meanwhile, only one chamber experiment from isoprene oxidation (in Fig 5a and Fig 6) was compared to the yield of isoprene in flow reactor experiments. However, isoprene SOA yields were also reported in other experiments, e.g., Kroll et al., (2006) found a yield range of 0.9%-3.6% for isoprene oxidation (low NO conditions) in chamber studies, which is lower than the chamber yield (~5.5%) used in this study and similar to the yield range in the PAM. A more comprehensive summary of published chamber yields should be included. Alternatively if there are reasons to exclude certain chamber studies, these should be given.

On a related point, what do the one-sigma uncertainties represent in Fig 5? Please clarify. As is, they may lead readers to assume they represent the uncertainty in the OH exposure (which is almost certainly much larger). They more likely represent ONLY the propagated variability from the measurements used to calculate it (rather than uncertainty in the offline/online calibration and/or models use to estimate  $\text{OH}_{\text{exp}}$ ). An uncertainty analysis should be conducted to characterize the true uncertainties in  $\text{OH}_{\text{exp}}$ , which would help clarify whether the differences in yield in Fig 5 really have meaning.

Table 1 and Figs 1-4 show that 8 different compounds were studied, however the yields are only discussed for 3 compounds. Why? Given that the yield results will likely be of the most interest to the community from this study, it would seem useful to discuss those results. This would give a better sense of the variability in the agreement/disagreement and provide better support for any generalizations and conclusions. As is, a reader quickly skimming the abstract and figures will assume that the yield conclusions broadly apply to the relatively wide range of compounds studied, which in current form is not supported in the manuscript.

### **3. Other topics:**

OA concentrations have a major effect on SOA yields (as the authors point out as background in Sect. 3.4). However, the OA concentrations in the PAM vs chamber experiments in Fig 5 are not discussed in terms of their effect on the measured SOA yields. At least some of the chamber studies report OA-dependent yields, and the chamber yields should be corrected to the same OA concentrations observed in the flow reactor experiments.

We suggest that Fig 7 should be plotted vs seed surface area, rather than mass, since condensation to seed aerosol or reactive uptake to an acidic seed aerosol would likely be a surface area-limited process.

Furthermore, it seems from the manuscript that the sulfuric acid ( $\text{H}_2\text{SO}_4$ ) seed aerosol was produced by oxidation of  $\text{SO}_2$  concurrent to isoprene oxidation in the flow reactor, in contrast to the atomized ammonium sulfate seed. Nucleation and atomization likely produced very different size distributions and thus very different surface area/mass ratios, potentially affecting the yields of SOA from isoprene. Also the size distribution in the nucleation experiments may lead to a significant fraction of SOA mass being too small to be measured by the AMS. The SMPS measurements from these experiments may help answer these questions.

Comparison of the mass spectra in Fig 2 is very unclear. Larger log-log scatterplots, difference plots, or uncentered  $R^2$  (Ulbrich et al., 2009) may be more useful. This topic was also alluded to by both referees.

Particle wall losses in the reactor are quoted as 32% +/-15%. This is much higher than in our experience, where these losses are typically 5% in mass, when using an aluminum wall

chamber. We observed losses of ~30% when using a glass cylindrical chamber as used in this study. As reported in Ortega et al., (2013), we believe the increased loss is due to nearly complete loss of charged particles to walls made of insulating material such as glass, Pyrex, or Teflon. In addition, very different charged-particle loss corrections need to be used when generating (charged) particles from an atomizer or (uncharged) particles by nucleation. Freshly atomized particles tend to be highly charged leading to even higher losses, and this effect can be reduced by passing the particles through a sufficiently potent radioactive neutralizer. It should be stated whether such neutralization was done or not in this study, so that it can help compare the likely particle losses in the experiments reported here with other studies. We suggest that the authors discuss these issues in some detail, as otherwise other groups may not be aware of the difference and apply the wrong loss correction in the future, thus significantly over or underestimating these effects.

Page 30588, lines 4-12. The authors briefly discuss the time required for condensation, noting timescales of 2000-20,000 seconds, while the residence time in the reactor is 100 s. If those timescales represent e-fold timescales, that would suggest only 0.5-5% of the condensable products would condense in the reactor, rendering the PAM useless without large seed surface areas, which is clearly not the case. For example, if the isoprene yield was corrected by that condensation efficiency, SOA yields of ~60-600% would be implied. A more detailed discussion (including explicit calculation of the condensation timescales) is needed.

Seed experiments were shown only for isoprene, which is the only compound with evidence for lower yields in PAM compared to a chamber experiment. However, the authors conclude at the end of Sect. 3.5 “these measurements suggest seed particles are required in flow reactor measurements in order to more closely simulate condensation conditions in environmental chambers.” Such a general statement is not supported and should be modified accordingly.

This comment grew out of a journal club discussion in our group, and was jointly redacted by Doug Day, Brett Palm, Amber Ortega, Zhe Peng, Weiwei Hu, and Jose-Luis Jimenez.

#### **References:**

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