

AMT Paper Reviewer #1 Response

1. Although it is true that the hypotheses of the studies cited in the introduction do not align with the motivation of our study, the reason for citing these studies was to highlight the typical methodology for VOC injection in batch-mode atmospheric chamber SOA experiments. Unfortunately, to the authors' knowledge, there are no existing reports on the systematic study of variability introduced in chamber measurements due to the method of VOC injection. The authors did not intend for the reader to draw direct correlations with these previous studies, as their motivations were quite different from those of our current report. Additionally, no motivation or parallels are drawn specifically to field measurements of SOA. The prime motivation of our work was to develop a simple, yet effective, means of increasing the repeatability of chamber SOA measurements that could be easily adopted by other researchers. Therefore, by addressing these previous studies, we sought only to demonstrate the typical, or "conventional" procedure for VOC injection, thereby highlighting the main focus of our study, which was the implementation of the stop/flow valve and split valve onto a conventional injection setup to improve repeatability.

2. a/b. As there is a continuous flow of dry, particle-free air directed through the flask and into the chamber/split valve throughout the course of the experiment, it is assumed that all of the α -pinene injected is volatilized and transferred to the desired location. Therefore, for direct injection experiments, it is assumed that all α -pinene is transferred to the chamber; whereas for split injection experiments, it is assumed that upon entering the split valve, the ratio of α -pinene that is transferred to the chamber vs. waste is proportional to the ratio of air to the chamber vs. air to waste (measured prior to the experiment on the Gilibrator 2 bubble generator). The authors do not have the instrumentation necessary to quantify the mixing rate nor the absolute mixing ratio of VOC in the chamber. Nonetheless, this was not the focus of this work. Despite not having quantified all chamber parameters (such as wall losses of particles and gases, mixing rate, etc.) nor been able to determine the contribution of each to the repeatability of measurements, the results presented here give an upper limit to the repeatability obtainable by making a very simple modification to the VOC injection method. In other words, we know that inclusion of this modification enhances repeatability significantly over conventional methods, but it does not, by any means, represent the best possible. We agree with the reviewer that quantitative knowledge of other chamber parameters that could contribute to measurement variability could improve measurements further.

2. c. For this work, the ozone was injected and allowed ample time to mix (10 – 15 minutes) prior to the injection of α -pinene. Although we do not report the calculations of gas partitioning to the chamber walls, we use the particle number concentration, SOA mass, and particle geometric mean diameter as a metric to demonstrate *repeatability*. Specifically, for the fully optimized injection setup, since the variation between replicate experiments (relative standard deviation, RSD) was significantly lowered for both 50 ppbv α -pinene (RSD for N_{\max} , $C_{\text{SOA, max}}$, and GMD_{\max} were all $\leq 3.5\%$) and 10 ppbv α -pinene (RSD for N_{\max} , $C_{\text{SOA, max}}$, and GMD_{\max} were all $\leq 7.8\%$), it can be assumed that the contribution of other variables, like VOC/O₃ mixing and gas-phase VOC partitioning to the chamber walls, to repeatability enhancements would be less significant. Again, the motivation of the current work was not to fully characterize the chamber, but rather to enhance the repeatability of common measurements made in SOA experiments (that is, particle number density, geometric mean diameter and mass loading).

2. d. The authors agree that the absence of seed particles may not represent atmospheric conditions in some cases, but in others, for example the pristine environment, seed-less conditions are wholly appropriate. In any case, seed-less experiments were used for several reasons, including the assumption that they would present the worst-case scenario for repeatability of SOA production specifically for the reasons outlined by the reviewer.

3. a. All experiments were performed under ambient temperature (21 +/- 2 C) and atmospheric pressure in the UVMEC (8 m³ Teflon chamber). For all experiments, the relative humidity was 0.0 % (as measured by a Vaisala TMH130 probe).

3. b. Due to extensive flushing with dry, particle-free air between replicate experiments (overnight flushing or two hours between same-day experiments), the background sampling of the UVMEC showed no particles present in the atmospheric chamber prior to the injection of the VOC for most experiments. At the very least, background particle number concentration was < 10 particles cm⁻³ before VOC injection.

3. c. For the eight experimental sets regarding the repeatability of replicate batch-mode chamber experiments (see **table 1**), α -pinene was the sole VOC used. Prior to this investigation on repeatability, various carrier gas flow rates were tested to compare the particle number and SOA mass yield from the same mixing ratio of *cis*-3-hexen-1-ol (HXL). Based on the results from **figure 3**, a carrier gas flow rate of 2000 mL min⁻¹ was implemented as standard procedure for all SOA

experiments performed in the Petrucci Research Laboratory at The University of Vermont. Therefore, when investigating the repeatability of replicate chamber experiments with α -pinene, the justification for specifically using an injection flow rate of 2000 mL min^{-1} stemmed from our previous work with HXL.

3. d. To the authors' knowledge, there are no reports in the literature addressing the quantitative repeatability of smog chamber SOA measurements. There are a very limited number of studies that include replicate measurements of SOA produced from α -pinene and O_3 . For example, Caudillo et al. (2021) performed four replicate α -pinene-derived SOA experiments but assumed a 30% uncertainty based on a study by Dada et al. (2020, which did not use α -pinene as a VOC). Furthermore, Caudillo et al. used a 26.1 m^3 stainless steel cylinder chamber and performed these experiments at $-30 \text{ }^\circ\text{C}$, which cannot be directly compared to our batch-mode atmospheric chamber experiments. In addition, a study conducted by Bonn et al. (2002) reported an RSD of 17% and 18% for maximum particle number and maximum volume concentration, respectively, at mixing ratios of 50 ppbv α -pinene and 110 ppbv O_3 . These uncertainty values decreased to 9% and 10% with mixing ratios of 1 ppmv α -pinene and 500 ppbv O_3 . However, these experiments were performed in a 0.57 m^3 spherical-glass vessel, and the authors did not report the number of replicate experiments performed. In a study conducted by Jonsson et al. (2006), for five replicate experiments at 19 ppbv α -pinene, the RSD for maximum particle number and maximum SOA mass was 14% and 21%, respectively. Yet, this was conducted in a 140 cm-long Pyrex glass flow tube (volume of 9.5 dm^3), which is not directly comparable to our measurements. Lastly, in a study conducted by Yu et al. (2011), replicate measurements (> 3) of 350 ppbv α -pinene ($0.5 \text{ }\mu\text{L}$ in a 0.216 m^3 chamber) had reported RSD values of $< 10\%$ for both particle number and SOA mass. This study also included the use of a stop/flow valve, however, the mixing ratio used (approximately 350 ppbv) was significantly higher compared to the mixing ratios used in our study.

4. The authors are fully appreciative of the need for high concentrations/mass of reaction products in current chamber experiments due to analytical limitations of current instruments. However, the significance of this work is to demonstrate that simple changes to conventional VOC injection in batch-mode chamber experiments could significantly reduce the variation in typical particle metric measurements for replicate experiments. Although the difference in RSD (across all particle

metrics) from conventional to fully optimized injection setup is more significant for low (10 ppbv) mixing ratios, there is still a dramatic improvement for particle number concentration and geometric mean diameter for high (50 ppbv) mixing ratios. Although the use of low VOC mixing ratio poses other logistical problems (mass spectrometer sampling, understanding intermediate SOA products, etc.), the fundamental takeaway is that the optimization of a conventional VOC injection setup can be applied to laboratory studies that use high concentrations to decrease chamber-experiment variability. Ultimately, current instrumental limits will need to be improved in order to better understand SOA formation at atmospheric VOC mixing ratios.