

## RESPONSES TO REVIEWER #1

The authors thank the reviewer for his detailed and comprehensive comments that will help make the paper stronger. We address all the comments and suggested corrections as best as we can, below.

General:

**REVIEWER COMMENT #1:** *The authors constantly claim the novelty of their newly constructed chamber, yet fail to provide any experimental evidence that could help to identify any unique aspect of the current chamber setup. What new discoveries could potentially be produced by the NCAT chamber compared with all the other chambers that are also equipped to study BB aerosols?*

**AUTHOR RESPONSE:** The reviewer is right in indicating that there are numerous indoor smog chambers already constructed; however, we do not claim that the chamber itself is novel. What we consider unique and novel is the “Combustion-Chamber System”. Given the unique combination of our custom designed and built instruments and combustion aerosol generation system, our entire chamber system is better described as “Unique”. The following are unique qualities of our system: BB combustion and aerosol generation using a tube furnace to produce aerosols under controlled burning conditions (temperature, air flow, oxygen content, and amount of fuel burned) and the ability to clearly visually differentiate brown carbon (often formed at around 450-500 °C), Black Carbon (formed around 650 - 750 °C) and other forms (mixed brown/black carbon) at intermediate temperatures. Figure 1 shows the two extreme forms of carbon collected on filters. The generation and introduction of the soot particles into the chamber is described in line 194-197. The generation of soot particles and the introduction method, along with filter and impinger sampling and the integration of the chamber to the cavity ring-down/nephelometer system are not common arrangements, and we haven’t come across chambers used in this manner. Many chambers are difficult to clean and therefore the characterization for wall loss and light intensity is a moving-target. Our chamber can more easily have each of the FEP panels cleaned and replaced. We believe the entire system is novel, not just the chamber. There is more to say here about the “novel” nature of the chamber system: We have characterized this chamber with particles that are combustion particles from biomass burning and have expended efforts to fully document the characterization with this manuscript. This adds to the “novel” or more rare nature of the chamber in that many chamber characterization efforts are undocumented, which makes the chamber results suspect and uncertain. Other chambers have been characterized with simple experiments, which are incomplete or unsatisfactory for conducting experiments later with different particles, such as from biomass burning. These aspects of this chamber and Figure 1 will be included in the revised manuscript.

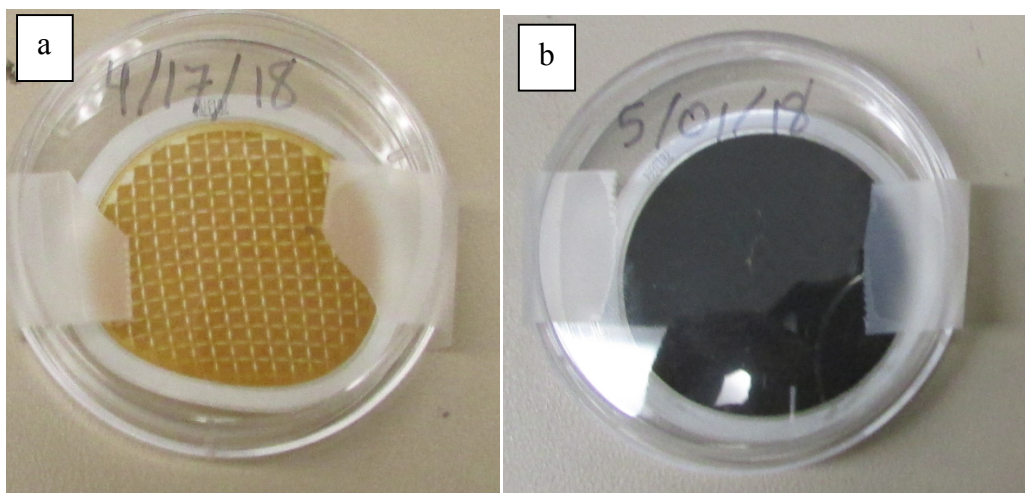


Figure 1. Filter samples of Biomass Burning aerosols produced in a tube furnace (a) at 450 °C b) at 800 °C. (Note the 800°C sample is highly concentrated)

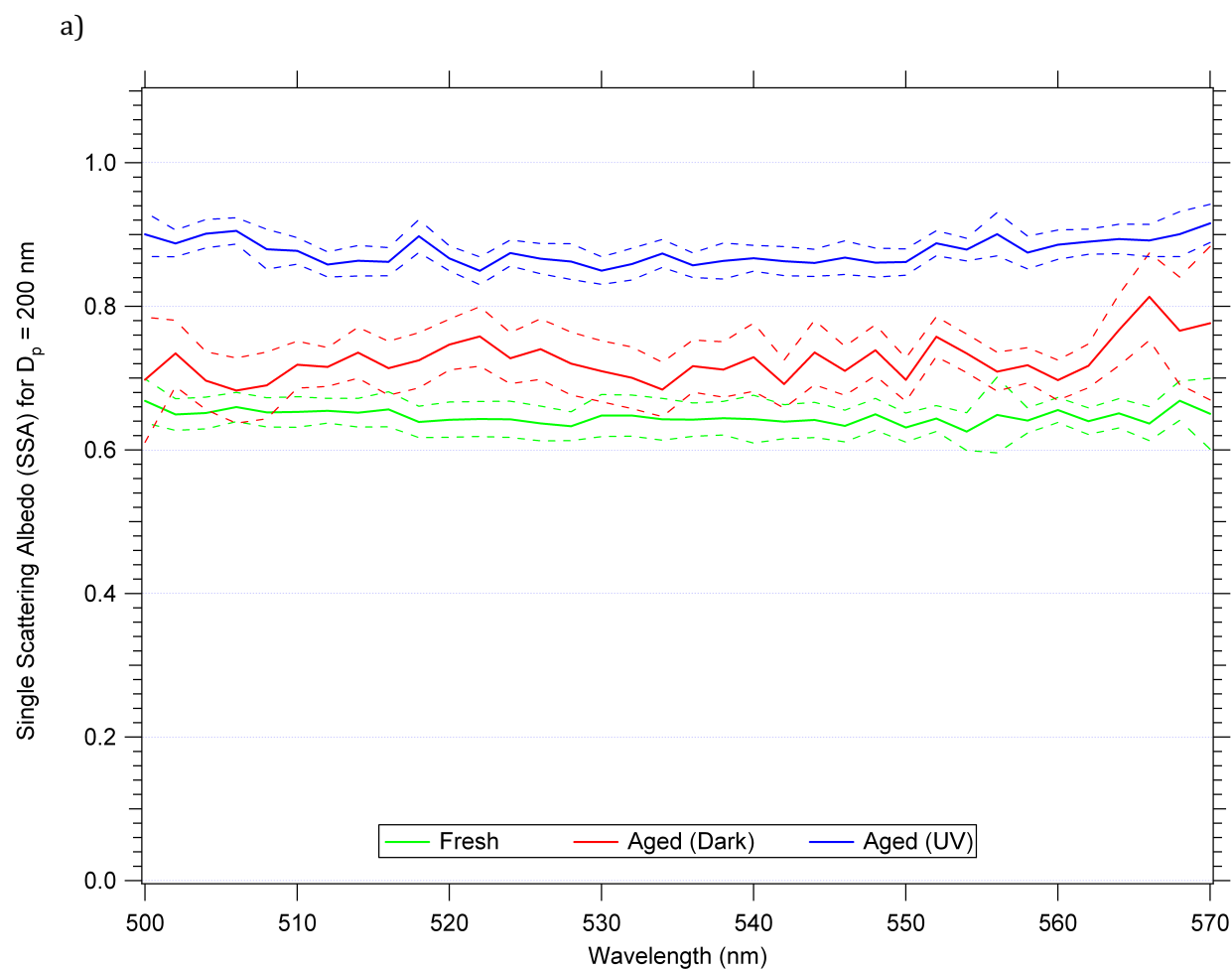
**REVIEWER COMMENT #2:** *One novel aspect of this chamber, as the authors state in the conclusion section, is ‘the use of a tube furnace ....., that enables the simulation of different burning stages ...’. However, the authors did not provide any experimental observations in terms of the physical, chemical, and optical properties of BB aerosols produced from different burning stages of a given fuel. Relevant measurements need to be added in the manuscript to support this claimed novelty of the chamber.*

**REVIEWER COMMENT #3:** *While the title highlights that the NCAT chamber is particularly suitable to study the aging processes of BB aerosols, the authors emphasize their focus on primary organic aerosols throughout of the main text. One illustration experiment that shows how photochemical aging would affect the optical properties of BB aerosols needs to be provided.*

**AUTHOR RESPONSE:** Comments #2 and #3 are related and the responses are combined. We will add preliminary measurements of average values of single scattering albedo (SSA) (Table 1) and SSA as a function of wavelength from 500 to 570 nm (Figure 4a, b, c) of BB aerosols produced by combusting African fuel samples (eucalyptus combusted in tube furnace at 500 °C) in response to comments and to make this section relevant. The plots show the single scattering albedo calculated from measurement of extinction and scattering cross sections. The measurements were conducted by sampling the particles soon after they were introduced into the chamber, after aging for 48 hours in the chamber in the dark, and after aging for 10 hours in the chamber with the UV lamps on. The measurements were done for three size bins (mobility diameters of 200, 300 and 400 nm).

**Table 3. SSA Values for Eucalyptus BB aerosol combusted at 500 °C.**

Particle Diameter (nm)	200	300	400	Peak Mobility Diameter (nm)
Fresh	$0.646 \pm 0.009$	$0.660 \pm 0.010$	$0.669 \pm 0.011$	131
Aged (Dark)	$0.729 \pm 0.028$	$0.712 \pm 0.021$	$0.720 \pm 0.029$	322
Aged (UV)	$0.877 \pm 0.017$	$0.923 \pm 0.016$	$0.960 \pm 0.020$	385



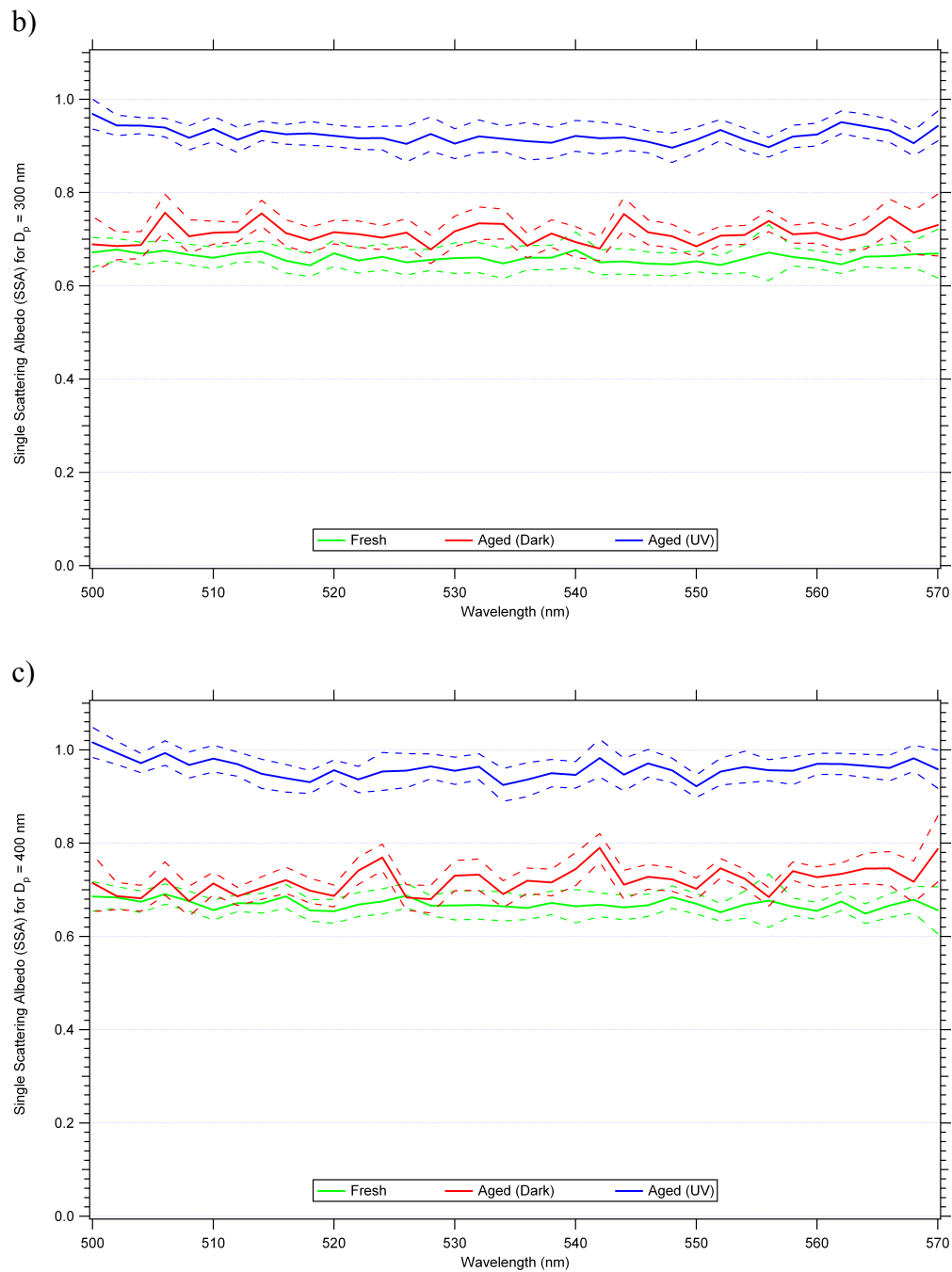


Figure 2. Single Scattering Albedo of Biomass Burning Aerosol obtained by combusting eucalyptus in a tube furnace at 500 °C. Measurement was done soon after introduction into the chamber and aging in the dark and with UV lamps on a) 200 nm particles b) 300 nm particles and c) 400 nm particles.

**REVIEWER COMMENT #4:** *The authors spend an entire paragraph in the introduction section discussing the need to investigate the effect of relative humidity on the evolution of BB*

*aerosols. Can relative humidity be well controlled in the NCAT chamber? If so, the humidity effect on the SMPS measured size distribution of BB aerosols needs to be given.*

**AUTHOR RESPONSE:** We wanted to emphasize the need to investigate the effects of relative humidity on optical and chemical properties of BB aerosols, since determining the extent to which RH impacts absorption and scattering is part of our future work. Aerosols exposed to high humidity will change their chemical, physical, and optical properties due to their increased water content. This process has an important impact on the particles' ability to scatter or absorb visible light, and is highly relevant to combustion in specific regions and seasons in Africa. Our current goal is establishing baseline measurements under dry 0% RH conditions only. Future work will investigate the change in optical properties as a function RH in the chamber.

**REVIEWER COMMENT #5:** *A large body of discussions in the main text, such as air purification, chamber flushing and cleaning, light spectra shown in Figure 6, and temperature profiles shown in Figure 8, have been well established routine chamber operation procedures for many years and can be moved to Supplement. Experimental evidence needs to be given in Section 3.5 to support the statement 'the setup in our laboratory will allow us to sample particles directly from and chamber, and measure their size distributions and optical properties as a function of aerosol age'. As suggested earlier, one experiment that illustrates changes in the optical properties of BB aerosols as a function of photochemical aging needs to be given.*

**AUTHOR RESPONSE:** The reviewer is correct in stating that there is nothing new in the chamber operation procedure that is included in this manuscript. However, each chamber is unique and uses different light sources that need to be described. Extra care is taken in the air purification system by using a zero-air generator to remove all possible atmospheric pollutants to keep a clean chamber at nearly 0% RH for baseline measurements. The importance of documenting officially in a publication the description of these "basic" parts or systems of the chamber is critical in establishing the confidence in the results of experiments. Furthermore, the characterization of these parts and describing and documenting the characterization procedures and routine is critical and is NOT always well established and should not be moved to a supplement.

We also agree with the reviewer that supporting data to show changes in optical properties and size distribution as a function of aging is needed. While this is the focus of the work in our lab and detailed analysis will be presented in future manuscripts, we have included data to show the functionality of the system and to support the claims we have made in this work. See response to comment #3 and #2.

### **Specific:**

**REVIEWER COMMENT #6:** *Page 3, Line 87: Most static Teflon chambers are actually not ideal for studying aerosol aging. As the experiment proceeds, the Teflon bag volume will be continuously depleted, eventually leading to significant particle wall losses. A typical chamber experiment usually lasts for 24-36 hours, which equals to approximately one to two days of atmospheric OH exposure given the average OH concentration of  $\sim 10^6$  molecules  $\text{cm}^{-3}$  generated in the chamber.*

**AUTHOR RESPONSE:** The chamber is operated as a “batch reactor” having a fixed volume of 9 m<sup>3</sup>. The Teflon walls are somewhat flexible, allowing for small changes in volume during injections without a change in pressure. The reviewer is correct in that dark experiments generally happen over a 24 - 48-hour period, such as the ones performed by Kalogridis et al. (2018). The use of UV lights can allow some reactions to proceed faster. Our chamber can more easily have each of the FEP panels cleaned and replaced. The figures below show the chamber before it was covered with Masonite and some of the frames.



Figure 3. The NCAT Chamber. This can be added in the manuscript if the editor and the reviewer consider it useful.

The schematics of the individual FEP panel joints is shown in Figure 3.

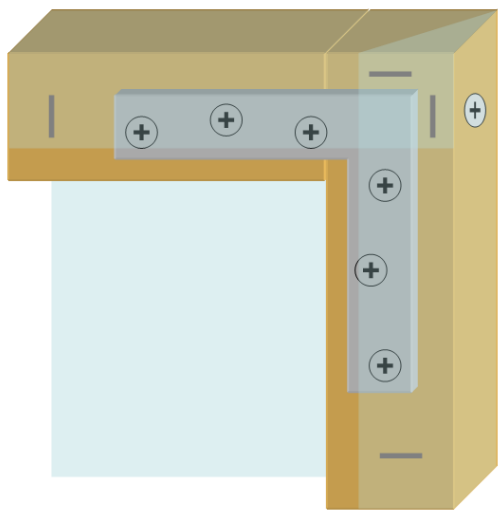


Figure 4. The corner of an FEP frame panel

**Reference:**

A.-C. Kalogridis, O.B. Popovicheva, G. Engling, E. Diapouli, K. Kawamura, E. Tachibana, K. Ono, V.S. Kozlov, K. Eleftheriadis; “Smoke aerosol chemistry and aging of Siberian biomass burning emissions in a large aerosol chamber; *Atmospheric Environment* **Volume 185**, July 2018, Pages 15-28

**REVIEWER COMMENT #7:** *Page 5, Line 165: Measurements need to be provided in the Supplement to support the statement ‘gas purity is less than ...and both methane and non-methane hydrocarbons’.*

**AUTHOR RESPONSE:** These specifications came from the manual for the zero-air generator. It is not independently verified. The text in the manuscript will be edited to reflect this.

**REVIEWER COMMENT #8:** *Page 7, Line 228-230: Have the authors tried to vary the atomizing pressure or use other solvents (e.g., acetonitrile) to dissolve impinger collected BB aerosols to see if these procedures would make a difference on the measured aerosol size distribution?*

**AUTHOR RESPONSE**

We thank the reviewer for this suggestion; however, this is outside the scope of this paper, as it has been shown elsewhere (Lewis et. al, 2009) that the structure of BB aerosol particles collapses under humid conditions. This is especially the case for impingement, which represents a supersaturated scenario.

**Reference:**

Lewis, K. A., Arnott, W. P., Moosmüller, H., Chakrabarty, R. K., Carrico, C. M., Kreidenweis, S. M., Day, D. E., Malm, W. C., Laskin, A., Jimenez, J. L., Ulbrich, I. M., Huffman, J. A., Onasch, T. B., Trimborn, A., Liu, L., and Mishchenko, M. I.: Reduction in biomass burning aerosol light absorption upon humidification: roles of inorganically-induced hygroscopicity, particle collapse, and photoacoustic heat and mass transfer, *Atmos. Chem. Phys.*, 9, 8949-8966, 10.5194/acp-9-8949-2009, 2009.

**REVIEWER COMMENT #9:** *Page 8, Line 275-280: How was the onset of gas chamber losses defined here? It seems like over the entire course of gas chamber loss measurements, standard gases are continuously injected into the chamber and withdrawn out of the chamber with a balanced flow rate. If so, uncertainties caused by chamber mixing timescale need to be considered. To fully isolate the effect of dilution on the measured gas wall loss rate, the authors are suggested to inject standard gases, turn off the injection flow and wait till well mixed, and then start the wall loss measurement.*

**AUTHOR RESPONSE:** The reviewer is correct. Wall loss measurements did not begin until concentrations of the gas had peaked and leveled off. Figure 3 only shows the injections of the gas to show how much time elapses between injection of gas and stabilization in the chamber. Figure 3 will be updated to show these injection times as vertical lines on the graph as shown below.

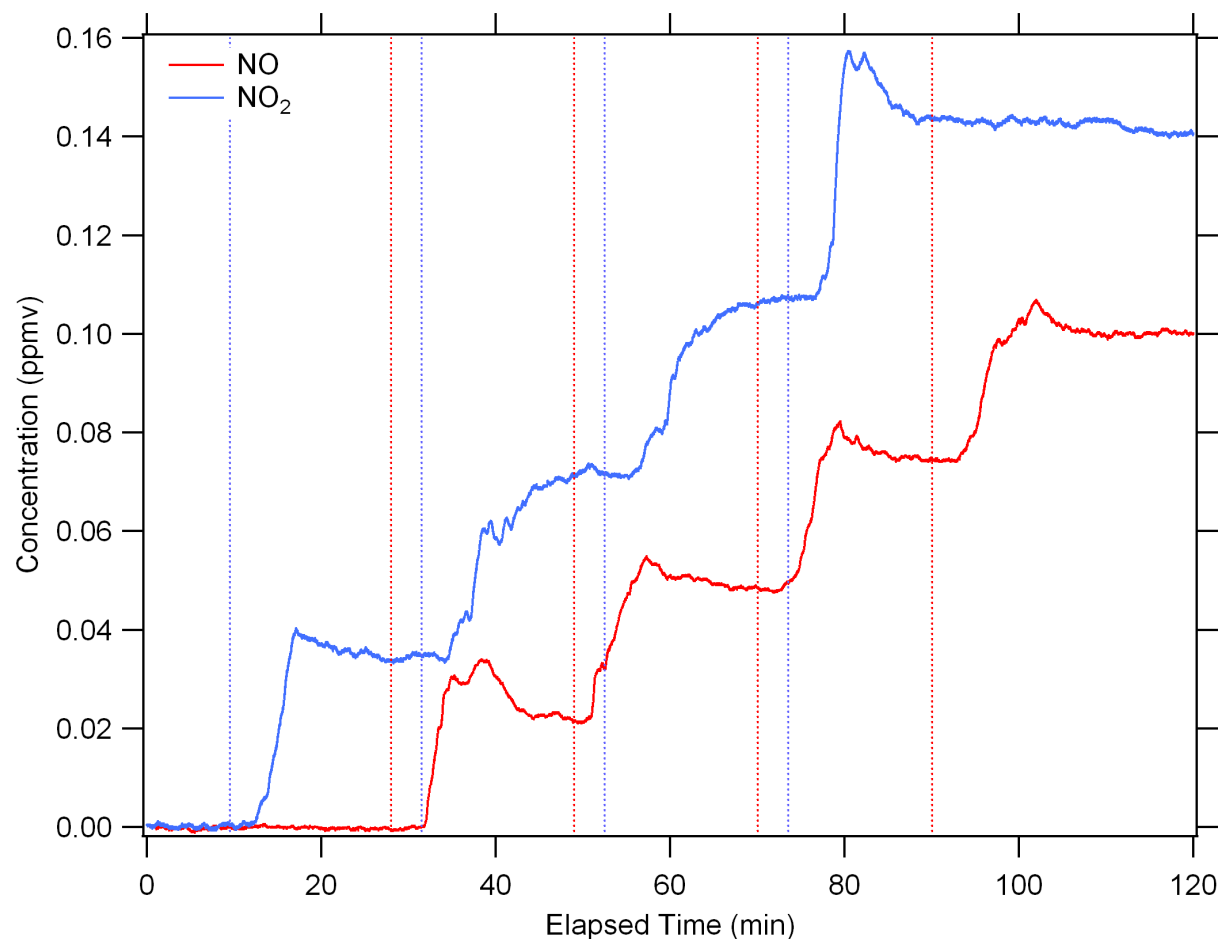


Figure 4: Injections and response (mixing) time for NO and NO<sub>2</sub>, done on different days, Vertical lines are injection times for NO and NO<sub>2</sub>. Injection time was 5 minutes each

Figure 4 in the manuscript shows what a typical wall loss looks like after the chamber is well mixed.

**REVIEWER COMMENT #9:** *Page 10, Line 338: Initial particle number concentration might be an indicator of the particle physicochemical properties, e.g., phase state. Understanding the relationship between initial particle number concentration and the loss rate needs to be included in the current study.*

**AUTHOR RESPONSE:** Certainly, it would be great to characterize for a range of sizes, and that can be suggested as future work. For this first manuscript, our reported work should be an adequate start, given the stated goals of the current project. There are more results to be published based on measurements being conducted on fuel sources from Africa. The size we picked is relevant, given the size distribution of combustion particles and availability of data



from cited references, which only provide wall loss for 100 nm particles. Also see response to comment # 11)

**REVIEWER COMMENT #10:** *Page 10, Line 346: When BB aerosols produced from a 500 °C furnace are introduced into a chamber operated at room temperature, organic vapors generated together with BB aerosols will undergo condensation on existing particles. On the other hand, organic compounds may evaporate from BB aerosols upon dilution in the chamber. So strictly speaking, the focus here is not POA.*

**AUTHOR RESPONSE:** The reviewer is correct in some sense. POA, previously treated as nonvolatile and nonreactive, can evaporate, oxidize, and re-condense to form SOA, which is known as aging of POA (Robinson, 2007). The cooling of particles upon introduction into the chamber can cause the semi volatile organics to condense on the particles. Due to the presence of semi- and low-volatile organics in the emissions, the freshly emitted particles from wood combustion are coated with organic matter (Tissari et al., 2008; Torvela et al., 2014). The coating often substantially increases due to the condensation of secondary organic matter formed either from anthropogenic or from biogenic organic precursor gases in the atmosphere (e.g., Akagi et al., 2012, Tiitta et al., 2016). So, in that sense the measured properties do not exactly represent fresh POA even in the field measurements. But, for measurements of fresh soot, the chamber is clean and free from typical atmospheric pollutants. The initial measurements are the closest we can get to POA before aging takes place, while not sampling hot, concentrated gases. Measuring the wall loss rate for organic compounds would be difficult with the current suite of available instrumentation, so it has not been performed in this work. However, we are collaborating with Dr. Surratt's Lab at UNC Chapel Hill for chemical characterization of filter samples collected at different stages. The results will be reported in upcoming publications.

#### References:

Robinson, A. L. *et al.* Rethinking organic aerosols: Semivolatile emissions and photochemical aging. *Science* **315**, 1259–1262, doi: 10.1126/science.1133061 (2007).

Tissari, J., Lyyränen, J., Hytönen, K., Sippula, O., Tapper, U., Frey, A., Saarnio, K., Pennanen, A. S., Hillamo, R., Salonen, R. O., Hirvonen, M.-R., and Jokiniemi, J.: Fine particle and gaseous emissions from normal and smouldering wood combustion in a conventional masonry heater, *Atmos. Environ.* **42**, 7862–7873, 2008.

Torvela, T., Tissari, J., Sippula, O., Kaivosoja, T., Leskinen, J., Virén, A., Lähde, A., and Jokiniemi, J.: Effect of wood combustion conditions on the morphology of freshly emitted fine particles, *Atmos. Environ.* **87**, 65–76, doi:10.1016/j.atmosenv.2014.01.028, 2014

Akagi, S. K., Craven, J. S., Taylor, J. W., McMeeking, G. R., Yokelson, R. J., Burling, I. R., Urbanski, S. P., Wold, C. E., Seinfeld, J. H., Coe, H., Alvarado, M. J., and Weise, D. R.: Evolution of trace gases and particles emitted by a chaparral fire in California, *Atmos. Chem. Phys.*, **12**, 1397–1421, doi:10.5194/acp-12-1397- 2012, 2012

Tiitta, P., Leskinen, A., Hao, L., Yli-Pirilä, P., Kortelainen, M., Grigonyte, J., Tissari, J., Lamberg, H., Hartikainen, A., Kuusalo, K., Kortelainen, A.-M., Virtanen, A., Lehtinen, K. E. J.,

Komppula, M., Pieber, S., Prévôt, A. S. H., Onasch, T. B., Worsnop, D. R., Czech, H., Zimmermann, R., Jokiniemi, J., and Sippula, O.: Transformation of logwood combustion emissions in a smog chamber: formation of secondary organic aerosol and changes in the primary organic aerosol upon daytime and nighttime aging, *Atmos. Chem. Phys.*, 16, 13251-13269, <https://doi.org/10.5194/acp-16-13251-2016>, 2016.

**REVIEWER COMMENT #11:** *Page 23, Figure 5: Please also provide the measured particle wall loss rate as a function of the particle diameter.*

**AUTHOR RESPONSE:** We have demonstrated that 100 nm particles (those with the shortest chamber lifetime, and far smaller than we plan to use for optical characterization) persist for sufficient periods to enable their collection and/or optical measurement. We have not presented size-dependent wall loss rate constants in this work, nor have many others. The stated goal of this work is optical property characterization. If we were to determine SOA yield or combustion emission factors, such size-dependent wall loss rate constants would be necessary, and we would perform that level of characterization should we expand to those goals. However, it is not necessary for our current purposes. In short, there is no step in our data analysis where a particle wall loss rate constant would be used, so measurement of size-dependent wall loss rate constants is not currently useful. However, the comments may be significant if only the reviewer explained why he thinks the amount of characterization results are insufficient. The reviewer has not specifically stated what they feel is missing from the manuscript.

**REVIEWER COMMENT #12:** *Page 27, Table 1: What type of detector is attached to GC for the identification of hydrocarbons?*

**AUTHOR RESPONSE:** The detector is a Flame Ionization Detector, and this will be inserted in the revision. Other details will be included. A dual column isn't a typical configuration, and should be included.