

## **Response to Reviewer 1**

We thank the reviewer for raising a number of important points, which are addressed in detail below.

### **General Comment**

I have several major concerns relating to the work. It is a little unclear what the potential of the instrument is in terms of adding new scientific understanding on organic aerosol (OA). For example, two of the major results from this study are that: volatility decreases with increasing oxygen content of the OA, and oxidation tends to move the OA from SV-OOA towards LV-OOA space. Both of these findings have been known for several years. Using PMF the OOA is separated into four factors based on reactivity and volatility, but it is also a little unclear what this provides in the way of new insight into OA formation or characteristics.

An additional finding was that the biogenic SOA was extremely volatile, with 10-25% evaporating with only a 4 °C temperature increase. I have serious reservations about this conclusion: there seem to be fundamental problems with the instrument, instrument characterization, and data interpretation that will need to be addressed in order for the work to be published. All of these issues are addressed in detail below.

### **Response**

While we fully agree that oxidation is generally known to move OA from SV-OOA-like to LV-OOA-like aerosol, the timescales over which this occurs and the inherent mechanisms are not well characterized at all. The measurements in this paper directly address these issues. Further, for ambient aerosol such movement in the OOA-space must generally be inferred from complex datasets in which the relative effects of different sources, atmospheric reactions, and partitioning are frequently hard to segregate. In the current study, the oxidation processes are directly controlled, simplifying the system. The volatility/reactivity description uniquely accessible by TPOT PMF is discussed further below in response to Comment 9, while temperature/SOA volatility issues are discussed further in response to Comments 1-3. We will insure that these points are made in the revised paper.

### **Comment 1**

The first and most significant deficiency I see relates to the temperature increase in the TPOT, which is given as “~4 °C”. This temperature increase is due to heat given off by the UV lamp. How constant is this 4 °C increase? Since it relates to the lamp, and is not controlled (i.e. by thermocouples), surely this temperature difference changes with ambient temperature? Is the temperature inside the TPOT continually monitored? This  $\Delta T$  should be plotted as a function of ambient T (at the very least in the Supplemental, but since this is a first description of the instrument, it is probably appropriate for the main paper). Then, the  $ORG_{AmbHt}/ORG_{Amb}$  ratio should be plotted as a function of this  $\Delta T$ .

### **Response**

The temperature was measured by a thermocouple mounted inside the lamp housing (i.e. closest surface to the lamp encountered by ambient aerosol), approximately 2.5 cm from the exit flange, placing it just beyond the end of the lamp. It is possible that axial or radial temperature gradients exist within the TPOT that are not fully reflected in the measured temperature. This will be discussed in the revised manuscript.

Further, the temperature increase reported in the original manuscript was the difference between the indoor temperature at the sampling site and this measured TPOT temperature ( $\sim 4$  °C). However, it is possible that the aerosol does not reach room temperature before entering the TPOT, and that the temperature difference should instead be calculated as the difference between the TPOT and outdoor ambient temperature. In this case, the temperature increase would be  $10.4 \pm 2.1$  °C, with a slight inverse dependence on the outdoor ambient temperature. A plot of this relationship will be added to the Supplement. Temperature was not monitored continuously, but was measured when switching from Amb to AmbHt conditions. The  $ORG_{AmbHt}/ORG_{Amb}$  ratio shows no dependence on the  $\Delta T$ .

### **Comment 2**

As stated above, the evaporation of 10-25% (average of  $\sim 15\%$ ) of the OA due to a 4 °C temperature increase is suspect. This would suggest an extremely volatile SOA, however, there may be other factors aside from heating that contribute to this decrease.

- a. Why is it assumed that the 254 nm UV will not have any effect on the OA (Pg. 8193, ln. 1-3)? Species like organic peroxides will definitely be lost to photolysis (and at this remote location, organic peroxide formation may be favored since the SOA formation is occurring under low  $NO_x$  conditions).
- b. What is the flow rate of the humidified nitrogen and  $N_2/O_2$ ? This will dilute the ambient sample and may cause evaporation of the organic aerosol by itself. With the instrument setup shown in Figure 1, this issue would not be detected. This seems like a potentially important shortfall of the instrument and needs to be discussed in detail.
- c. As is standard procedure for characterizing any thermodenuder, particle losses through the 3-way valve need to be quantitatively described using an aerosol like NaCl or  $(NH_4)_2SO_4$  and CPCs or SMPSs located upstream/downstream of the 3-way valve. Particle losses through both the reaction channel and the bypass channel need to be characterized since differences may be wrongly interpreted as higher evaporative losses than are actually occurring.

### **Response**

(a) We agree that photolysis of organic peroxides is a likely contributor to the observed mass loss (as stated in the original version of the ACPD paper, at the top of page 8193). However, we will make this point stronger in the revised version. To reflect this uncertainty, the labeling scheme for lamp-affected TPOT conditions will be changed from AmbHt and AmbHtOH to AmbUV and AmbUVOH. (b) We agree that dilution of the sample by the humidified  $N_2/O_2$  flow may cause evaporative losses. However, note from Fig. 1 that this dilution occurs before the bypass/reaction zone split. Therefore such dilution-induced evaporation would occur equally in the bypass and reaction pathways and cannot contribute to the observed mass loss. (c) Wall loss experiments through the

reaction zone were conducted with the UV lamp on, using size-selected BES particles. These experiments show ~100% transmission between 100 and 300 nm mobility diameter (larger sizes were not tested), with ~90% transmission for 50 nm particles. While losses through the 3-way valve were not characterized, the bypass and reaction pathways are identical in this region. Thus it is very unlikely that differences in bypass vs. reaction wall losses significantly contribute to the observed mass loss.

### **Comment 3**

It appears that interpolations between sampling periods were up to 3-4 hrs. How much uncertainty does this introduce when calculating ratios to ambient concentrations (i.e. in Figures 3 and 6)?

### **Response**

Fig. 6 is constructed from the difference between the AmbHt and AmbHtOH conditions, which are alternated with a period of 12 min in each mode (Page 8189, line 4). This period is faster than the observed fluctuations in aerosol properties during the campaign and we do not expect significant uncertainties to be introduced.

On the other hand, Fig. 3a is constructed by interpolating OA concentration over several hours. Fortunately, the sampling site is rarely influenced by significant local emissions, but rather by daily temperature/boundary layer cycles and major changes in weather patterns/air mass origin. Thus while a 3-4 hr interpolation is not ideal and may contribute somewhat to the vertical scatter in Fig. 3a, we do not expect it to greatly affect the results. Note that despite the scatter, Fig. 3a indicates consistent results are obtained despite experiments being performed on many different days and different periods throughout the day. Note also that this consistency is evident through visual inspection of Figs. 2 and 9.

### **Comment 4**

Are there any artifacts induced by subjecting the samples to the equivalent of 1-10 days of oxidation in about 1 min? Other studies are cited in the paper and have used a similar approach, but this needs to be discussed. The PMF results seem to suggest that there may be some artifacts due to the high oxidant levels. For example, the factor  $OOA_{R,NV}$  is identified from TPOT analysis as a species that does not volatilize with the temperature increase, but reacts readily with OH (as shown by the significant decrease in Figure 11). In Figure 11, this factor is shown to decrease, even at OH exposures of less than 1 day (average decrease appears to be a factor of ~0.5). However, on July 21, this factor significantly increases under high OH conditions over the course of ~12 hr. The factor  $OOA_{P,NV}$  – which increases significantly in the TPOT due to OH exposure seems to show only a slight increase on July 21?

### **Response**

All experiments in which the particles were exposed to OH are shown in Fig. 11. The figure shows that OH exposure always causes a decrease in  $OOA_{R,NV}$  and an increase in  $OOA_{P,NV}$ . The behavior noted by the reviewer is not in evidence. (Data collected on July 21 comprise the points at OH exposures of  $1.08 \times 10^{12}$  and  $1.48 \times 10^{12}$  molec  $\text{cm}^{-3}$  s). Perhaps the confusion arises from the July 21 data in Fig. 12, in which the PMF factors

are shown only for the Amb condition, as noted in the caption? (Time series of July 21 OH exposures are not currently contained in the paper.)

**Comment 5**

Figure 9 is somewhat confusing. The individual panels in each figure are so small that it is difficult to interpret or gain anything useful from, even significantly magnified. Also, the Amb, AmbHt, and AmbHtOH periods are indicated by yellow, red, and blue shading, respectively. But the majority of time in each figure the shading is white – what is happening during this time?

**Response**

As noted in the caption, the shaded regions denote selected Amb, AmbHt, and AmbHtOH periods. Only selected regions were shaded (similar to Fig. 2) to avoid cluttering the figure, while still enabling the reader to compare the effects of different conditions. We will expand the Fig. 9 shading in the revised manuscript.

**Comment 6**

Pg. 8194 line 7-9: Re-condensation of evaporated OA is an important point. Most thermodenuders have an activated carbon section immediately downstream of the heated zone to deal with this issue – what is the residence time from the exit of the reaction chamber to the AMS inlet?

**Response**

The transit time is approximately 15-30 s.

**Comment 7**

Figure 9a: why does the BBOA factor increase throughout the day during a period not influenced by biomass burning?

**Response**

It is likely that the BBOA factor does not represent “pure” BBOA, but is somewhat mixed with other OA sources. This is discussed in more detail in response to Comment 9 by Reviewer 2. Briefly, the biomass burning period exhibits high residuals in the PMF solution. Additionally, the mass fraction of  $m/z$  60 in the BBOA factor is less than measured  $f_{60}$  values for the total organic aerosol during this period. This suggests that the BBOA factor is somewhat mixed. This outcome is not surprising given that biomass burning influences only briefly influences the site and thus a poor BBOA fit does not greatly increase the Q-value.

**Comment 8**

Pg. 8194, line 22: give wall surface area-to-volume ratio in the TPOT.

**Response**

The surface area/volume ratio is approximately  $1/3 \text{ cm}^{-1}$ .

**Comment 9**

Pg. 8199, line 17-18: It seems that the mass spectral variability in the TPOT data set is governed by volatilization and OH oxidation AND by factors such as transport, source location + strength, atmospheric reactions, etc. This would seem to make interpretation of the TPOT PMF analysis at least as complicated since the aerosol sources/age are obviously not constant.

### **Response**

We thank the reviewer for raising this point as it provides a useful discussion point regarding future TPOT-like analyses. The complexity of the analysis depends greatly on the details of the PMF application. The crucial point is that the TPOT PMF induces volatility/oxidation-based variability in the mass spectra, which is not accessible using conventional PMF. The present study was conducted in a region dominated by a single source class (biogenic SOA), which simplifies the analysis. While other locations may have more source complexity, it is not necessary to apply PMF to an entire dataset at once. At the discretion of the scientist, periods characteristic of particular source/aerosol types can be analyzed separately (e.g. if biomass burning periods were more prevalent during the current campaign, it would be logical to perform separate TPOT PMF analyses of biogenic and biomass burning-dominated periods; unfortunately, the biomass burning period was too short to provide adequate statistics). For each period segregated in such a way, volatility/oxidation-based variability remains, and one would expect these properties to be reflected in the PMF solution. We will clarify this point in the manuscript.

### **Comment 10**

Pg. 8201, line 18-19: “~3 days of photochemical aging” say instead “3 days of simulated photochemical aging” (other points throughout the paper as well – e.g. pg. 8201, lines 24, 25, and 28; pg. 8205, line 7-8). Alternatively, use ‘day-equivalents of aging’ as in pg. 8202, line 2-3.

### **Response**

We will adopt “day-equivalents of aging” in the revised manuscript.

### **Comment 11**

Pg. 8192, line 19-27: The range of O<sub>3</sub> levels in the reaction chamber should be given.

### **Response**

O<sub>3</sub> concentrations ranged from 40 to 1100 ppbv.