Review of Slowik et al., ACPD, 2012
"Real-time, controlled OH-initiated oxidation of biogenic secondary organic aerosol"

General Comments:

This paper describes a new instrument (the Toronto Photooxidation Tube - TPOT) that subjects an aerosol sample to gentle heating and oxidation by OH, followed by AMS analysis. The instrument was deployed in the summertime in a remote forested site in Canada. PMF analysis was applied to the data to gain additional insight into the volatility and reactivity of biogenic SOA. Overall, the paper is well-written and nicely organized.

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.

Specific Comments:

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 ΔT should be plotted as a function of ambient T (at the very least in the Supplemental, but since this is a first description of this instrument, it is probably appropriate for the main paper). Then, the ORG_{AmbHt}/ORG_{Amb} ratio should be plotted as a function of this ΔT.

2. As stated above, the evaporation of 10-25% (average of ~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 NOx 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.

3. It appears that interpolations between ambient 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)?

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?

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?

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?

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

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

9. Pg. 8199, line 17-18: It seems that 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.

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). Alternately, use 'day-equivalents of aging' as in pg. 8202, line 2-3.
11. Pg. 8192, line 19-27: The range of O_3 levels in the reaction chamber should be given.

Technical Corrections:

1. Pg. 8184, line 6: delete "unreacted"
2. Pg. 8202, line 17: delete "unreacted"
3. Pg. 8192, line 17: delete "both"