Summary

We are really thankful to the four reviewers who took the time to read the manuscript and provide insightful comments. This document contains responses to all the comments from the reviewers. We have considerably revised the manuscript in parallel with writing this response. For the sake of convenience, the reviewer's comments are reproduced below in *italic*, and are followed by our response and/or brief description of our revisions.

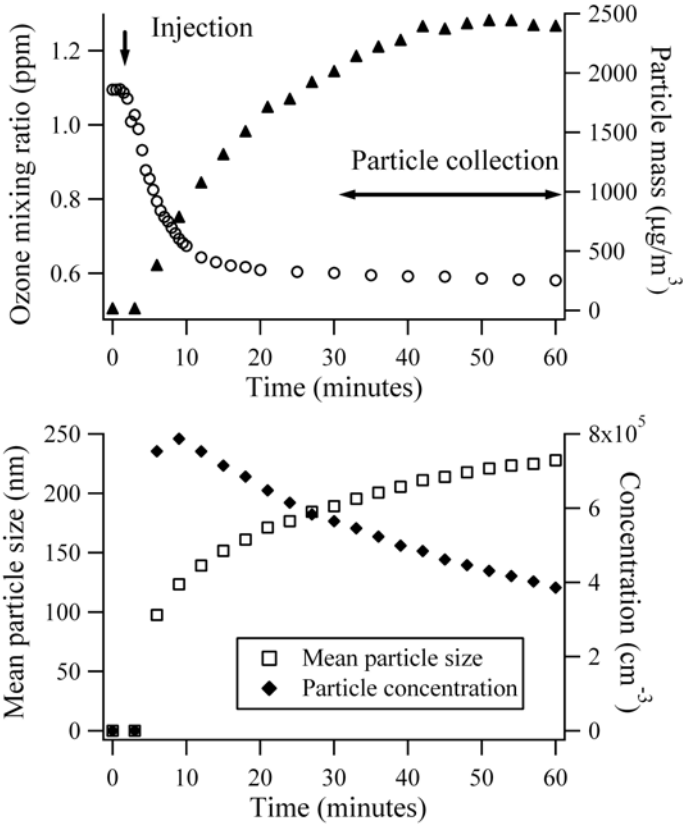
Response to Reviewer 1

In this manuscript the authors describe experiments in which volatile products from the irradiation of model SOA (secondary organic aerosol), generated from the ozonolysis of D-limonene, are observed using chemical ionization mass spectrometry. The wavelength dependence of the yields of these products tracks the absorption spectrum of the SOA material closely. The dominant observed photodegradation products are small (three carbons or fewer) oxygenated molecules such as acetaldehyde and acetic acid. The primary precursors responsible for these degradation products are proposed to be carbonyl- or carboxyl-containing species. Similar photodegradation products may also be generated from SOA produced from OH reactions, as well, since these will also lead to the formation of similar precursors.

The authors do a very good job of explaining the experiments and their analysis of the data. They do not overreach in their conclusions and explicitly state assumptions made, such as assuming that each product is ionized at the same rate. This manuscript should be published after the following points are considered.

Comment. *The particles are stated to be ∼ 100 nm at a concentration of* 8×10^5 cm^{-3} *after 10 minutes of reaction and then ∼ 220 nm at a concentration of* 3×10^5 cm^{-3} *after an hour. This represents a four-fold increase in particulate mass over this time span (not accounting for particle loss on the walls of the bag). How is the overall mass increasing by this much? It seems unlikely that it can be explained by additional ozone reactions since half of the ozone is already reacted after the first 10 minutes.*

Response: Measurement of SOA yields was not the primary objective of this work, and this is why we did not pay special attention to this particulate mass increase. In response to this comment we will include the particulate mass concentration in Figure 1. The new version of Figure 1 is reproduced here. The particulate mass does continue to increase after the initial decline of the ozone concentration. This can be attributed to: i) slow reactions of residual ozone with the first generation products; ii) slow accretion of semivolatile products by the particulate mass. Both effects have been documented in the literature (Ng et al., 2006;Barsanti and Pankow, 2004, 2005, 2006;Kroll et al., 2007). We have inserted these references in the manuscript.



***Comment**. What was the timescale for the drop in total PIC (product ion current) after the light was turned off? Comparing this timescale to the 5-20 minutes required for the PIC signal to reach steady-state values when the light was turned on could indicate whether the photodegradation occurred in a single step (in which case the PIC signal drop should be prompt) or through multiple steps (in which case these photo-initiated reactions could persist for some time after the light was turned off).*

Response. It took about the same time for the *PIC* to drop back to the original level after the lights were turned off (we added this sentence to the revised manuscript). Our explanation for the slow time scale is that the rate with which the photoproducts are coming out is limited by the evaporation rate from the SOA sample. If this is the case, the signal should not drop down to zero as soon as the radiation is turned off.

***Comment.** To determine the potential atmospheric significance of such photodegradation, the rate for volatile product formation should be estimated for typical actinic fluxes. Will such a process be competitive with reactions of the SOA with OH, O_3 or NO_3?*

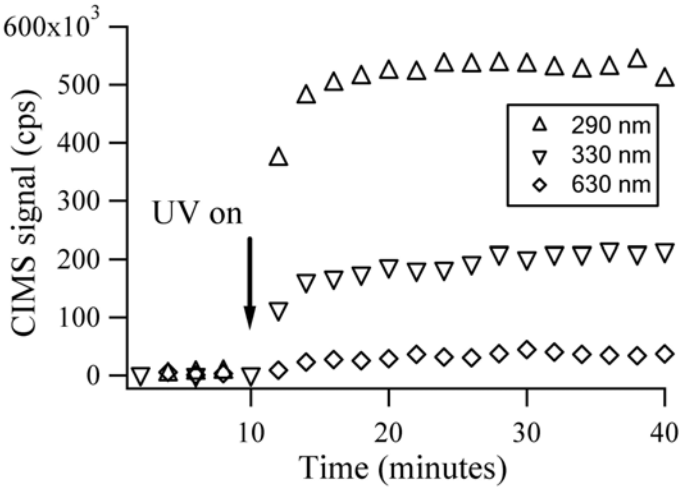
Response. In a paper published by our group lab recently (Mang et al., 2008), we estimated the lifetime of photodegradation of carbonyl functional groups in limonene SOA to be several hours for representative solar fluxes. We did not want to repeat the same estimation in this paper.

***Comment**. Is it possible that the findings from this study could explain some of the volatilization measured from OH-initiated reactions of organic aerosols and films by other researchers? More specifically, in those studies 254 nm light from mercury lamps is used to initiate ozone photolysis to create $O(^1D)$ which then reacts with H_2O to make OH radicals. The resulting products include carbonyl and carboxyl groups which may absorb the 254 nm light and lead to photodegradation just as observed in the present work.*

Response. This is an interesting possibility. If such experiments are not carefully designed, the 254 nm UV radiation may in fact cause some photodegradation of the oxidized organic film. The intensity of radiation capable of photochemical production of OH in quantities sufficient for the volatilization should also be capable of photolysis of molecules inside the film. We have done a limited number of experiments on photodegradation of organic films processed with OH or Cl in presence of O_2. Our preliminary measurements indicate that photodegradation of such films is not very efficient. We prefer not to include the discussion of these volatilization studies in this paper before we get more reliable data on the efficiency of photodegradation.

***Comment**. In Figure 7, why is the product ion signal so high (0.7×10^6 cps) before the UV lamp is turned on? This signal doesn't even double (at 290 nm) when the light is turned on which indicates that there is a significant dark source of these peaks (50-400 m/z). Hence, the photodegradation seems to be relatively minor compared to this dark source.*

Response. The total ion signal shown in Figure 7 consists of two parts: detector noise, which is about the same for all m/z points and the actual signal. The noise looks high is because it includes contributions from all data points between 50 m/z to 400 m/z (excluding water peaks). With 0.05 m/z point spacing, this corresponds to detector noise of about 1000 cps. This value is indeed too high for a channeltron detector. Our detector was on the brink of death during the measurements described in this manuscript. We have replaced it since then, and this reduced the noise level back to its normal value. The signal only comes from actual peaks appearing in the mass spectrum. As Fig. 4 demonstrates, peaks due to the products are clearly visible in the mass spectrum on top of a flat background . The high apparent background count in Figure 4 is therefore an artifact of the signal summation procedure. In order to avoid this confusion, we are going to subtract the noise background from the data shown in Figure 4 in the new manuscript. The updated Figure 4 is shown below. This is not going to affect the rest of the discussion.



Comment. *In Figure 10, is the normalized relative yield plotted the same normalized yield defined by equation 5? Or are these yields just normalized so that the results from the CRDS and CIMS experiments overlay one another?*

Response. We have added the following sentence to the caption of this figure: “Both spectra were normalized to 270 nm using Eq. (5).” This should help avoid ambiguities.

Response to Reviewer 2

***General comments**. The manuscript describes a study to measure photodegradation of limonene ozonolysis SOA using chemical ionization mass spectrometry. The authors' findings suggest that the photodegradation of biogenic SOA is not limited by the UV wavelengths and RO_2 + HO_2 or RO_2 reactions are the dominant route responsible for SOA formation under low NOx conditions. While the results are certainly interesting, this reviewer is concerned about the way the filters were sampled. Particularly the authors have used extremely high concentrations of precursor VOC for some experiments, most likely leading to absorption of gaseous species to quartz fibre filters. Have the authors considered the use of an annular denuder or alternatively impactor sampling? The potential influence of filter artefact formation needs to be clarified before it can be finally accepted for publication.*

Response. Before responding to this concern, we would like to emphasize that reactions of RO_2 with HO_2 or RO_2 are important under our experimental conditions; we do not claim that this is the dominant pathway for the generation of SOA in the atmosphere. We believe that adsorption of volatile species to the filter is not a very significant issue. If such absorption is reversible, the volatile products would be removed by purging the filter in dry nitrogen flow before the measurements start. Before the radiation was turned on, the CIMS instrument detected no volatile organic species coming off the filter. Even when the sample was gently heated to 40C, the CIMS spectrum remained clean. In case of irreversible chemisorption of volatile species by the organic matrix, we can regard the resulting products as realistic SOA species formed by accretion chemistry. We have modified the experimental procedure to include the following text: "All filtered samples were placed under a flow of dry nitrogen for at least an hour in order to remove volatile species that reversible absorbed onto the filter surface and/or SOA material. The filters were used within 10 hours of their preparation to avoid possible aging effects." We also added a new paragraph talking about these issues in section 3.4.

Specific comments.

Pp. 4728 L17: Please provide a reference for this number. There is a newer estimate available which the authors may want to cite. Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181-3210, 2006.

Pp. 4730 L25-29: This paragraph is redundant and not necessary for this manuscript.

Pp. 4731 L6: ultrahigh purity (UHP) oxygen -> ultra-high purity (UHP) oxygen

Pp. 4731 L7: This reviewer is unable to find an ozone generator named "Ozonetech OZ2SS". Please provide a full name of the manufacturer and the model for this device.

Pp. 4733 L22: What do the authors mean by "normally not observed"?

Pp. 4740 L5 and many places elsewhere: The ACP citation style should be followed. e.g by (Mang et al., 2008) should be by Mang et al. (2008).

Pp. 4741 L24: 7OH-limonaldehyde -> 7-hydroxy-limonaldehyde

Pp. 4743 onwards: This section is extremely densely written.

Fig. 11. limononic acid -> Limononic acid

Response. We have accepted and addressed all specific comments by this reviewer, including:

- adding the reference specified above
- removing the organizational paragraph at the end of the introduction section
- correcting all the typos
- including a full model number for the ozone generator, which, incidentally, is no longer sold by the company
- trying to make writing less “dense”
- fixing the style issues
- fixing the molecular names in the text and in figure 11

***Comment**. Pp. 4745 L21: Do the authors have evidence to back this statement up? 100 ppbv seems significantly higher than typical atmospheric concentrations of monoterpenes (<5 ppb).*
Response. The lowest limonene concentration we used was 21 ppb. We stated the concentration explicitly in the text, and weakened this statement to: “The lowest concentrations of reactants used in this study (100 ppb ozone; 20 ppb limonene) are still higher than the typical atmospheric values.”

***Comment**. Pp. 4760 Fig. 5: The authors may want to include the CIMS spectra for 0.1 ppm as well.*
Response. Unfortunately, we did not run this particular experiment at 0.1 ppm ozone.

Response to Reviewer 3

The authors present a study of the photodegradation of limonene SOA, along the lines of what they had done previously in Mang et al (2008) and Walser et al (2007). The unique aspect of this manuscript is the use of a chemical ionization mass spectrometer to characterize the volatile products, and some lower ozone and limonene concentrations were used. The paper is well-written and should be published in APCD after the following comments and questions are addressed:

Comment*. The authors state that the samples are stored under flowing dry nitrogen, and the photodegradation experiments are also carried out under dry nitrogen. This practice must cause the evaporation of all but the least volatile SOA products from the aerosol sample. I presume that the experimental motivation for doing this is to keep the background signal from semi-volatile material low so as not to interfere with the signal from the volatile degradation products. But the authors should discuss how this affects the atmospheric implications of their results.*

Response. Since we submitted this manuscript, we did some measurements of volatilization mass loss in limonene SOA deposited on a quartz crystal microbalance. Freshly prepared SOA samples do emit a number of low-molecular weight species at the beginning of purging (we have identified some of them with GC/MS). These compounds would not normally partition in the particle phase; they were reversibly absorbed on the filter because of the elevated concentration of organic reactants in the chamber. After this initial loss of the most volatile species, the volatilization mass loss slows down considerably. Fig.9 in the manuscript demonstrates that this evaporative loss from SOA is a very slow process; less than 10% of SOA material is lost to volatilization on a time scale of the measurements. We have considerably revised section 3.4 of the manuscript to emphasize this point.

Comment*. The authors should discuss how the intensity of their light source compares with the actinic flux that a typical aerosol particle will encounter in the atmosphere (this is related to point (3) raised by Anonymous Referee #1).*

Response. The radiation power ranged from 0.050 to 2.6 mW in these experiments. For comparison, the flux of solar radiation at the Earth's surface at 30° solar zenith angle between 300 nm and 310 nm is $\sim 4\times 10^{14}$ photons cm^{-2} s^{-1} (Finlayson-Pitts and Pitts, 2000); this corresponds to about 0.3 mW cm^{-2}. Therefore, the radiation flux to which the SOA material was exposed to was representative of daytime atmospheric conditions. We added this information in the manuscript.

Comment*. Do the authors have a sense of the rate of mass loss caused by photodegradation and thus how photodegradation will change the size of the aerosol over its lifetime?*

Response. We didn't quantify the mass loss due to the photodegradation. However, we are currently in the process of doing exactly that, using quartz crystal microbalance techniques. These experiments turn out to be quite difficult, and we are not yet in a position to present the results.

Comment*. How do the mass transfer limitations observed in your experimental setup (p.4738, line 18-19) compare to what would happen for an atmospheric aerosol particle?*

Response. We hypothesized in the text that "In actual atmospheric particles, the time scale for the release of the photoproducts should be considerably faster, especially for non-sticky molecules, where this time is limited by the diffusion across the particle."

Comment. *The authors should do a more thorough job of connecting the discussion of the mechanism on pp. 4743-4744 to the observed mass spectra*
Response. The point of the simulation was to explain the lack of dependence of the action spectra on the concentrations of ozone and limonene used for SOA preparation. The simulation demonstrated that over the concentration range used in this study, RO_2+HO_2/RO_2 chemistry is important, and therefore, there should be lots of carbonyls amongst the products. Connecting the simulation results to the mass spectrum of thermally desorbed SOA is more challenging. The mass spectrometer does not have enough resolving power to unambiguously assign the molecular formulas; not does it have MS/MS capabilities to get information about the structures of SOA constituents. In the future, we hope to be able to better connect the mechanism and mass spectra using higher resolution mass spectrometry approaches, e.g., by replacing the present mass spectrometer with a PTR-MS-MS system.

Comment. *p. 4731 line 4: Please provide more details regarding the Teflon FEP bags, in particular, what is their volume?*
Response. The Teflon bag volumes are listed on table 1. We will draw attention of the readers to this table by inserting additional references to it into the text.

Comment. *p. 4737 line 4-5: "only oxygenated species should be detectable by this instrument." I believe this statement is incorrect. See, for example, the review of PTRMS by Blake et al (2009).*
Response. What we meant was that we were likely to be much more sensitive to the oxygenated species. We changed the wording appropriately.

Comment. *p. 4732 line 5: "300 pm" should be "300 ppm"*
p.4741 line 6: "a very satisfying cross-validation result" please remove this commentary or use more technical language
p.4742 line 20: please remove the word "kinetically"
Response. All fixed now.

Response to Reviewer 4

The manuscript of Pan et al. describes the generation of photoproducts from the photochemical degradation of ozone-generated SOA from limonene. This work is an extension of previous work of the authors, bringing a new analytical technique (chemical ionization mass spec) to bear on the problem. The work is novel and will be of interest to the general readership of ACP. I suggest it is published, with minor revisions as indicated below:

Comment. *Page 4730: Is the final paragraph necessary (which describes the organization of the paper?)*
Response. It has been deleted in the revised version.

Comment. *Page 4737: proton transfer mechanism relies solely on the proton affinity of the target ... it is not necessarily true that only oxygenated species will be ionized.*
Response. The sentence has also been changed in revised version.

Comment. *Given your irradiation intensity, what would be the corresponding atmospheric irradiation time, i.e. does 5 minutes of experimental irradiation represent 1 hour of environmental exposure, etc.?*
Response. We have inserted a statement in the experimental section that compares the level of UV exposure under our laboratory conditions and typical atmospheric conditions. The conclusion of this comparison is that “the radiation flux to which the SOA material was exposed to was representative of daytime atmospheric conditions.” It is difficult to be more quantitative than that without specifying time of day, location, etc.

Comment. *How might experimental results change (and can you do the experiment at some future point?) if using humidifed air? It might help to explicitly state in the manuscript why dry air was necessary.*
Response. Dry air was not necessary for the SOA preparation part. The focus of this paper was on: i) method development; ii) concentration effects. Now that the method is developed, we can start exploring effects of different environmental parameters that may affect SOA composition and its photochemistry.

References

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