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Atmospheric
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Interactive comment on "Chemical aging of *m*-xylene secondary organic aerosol: laboratory chamber study" *by* C. L. Loza et al.

Anonymous Referee #2

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General comments:

This manuscript describes results from environmental chamber experiments conducted to probe the aging (chemical transformation) of secondary organic aerosol (SOA) from the photo-oxidation of m-xylene. The authors developed a new experimental protocol to extend the duration of typical chamber experiments by sampling with different groups of instruments (rather than all instruments) at different times of the experiment. They investigated the changes in OA composition (specifically elemental ratios such as O:C) and OA concentration over the course of photo-oxidation experiments lasting up to 36 hours. They find that O:C concentrations increase after the first 5 hrs of oxidation and that OA concentrations eventually start to decrease, indicative of fragmentation reactions. The manuscript is well and clearly written and reports new and interesting results that are within the scope of ACP. I recommend publication of the manuscript in ACP after my comments below have been addressed.

Major comment

I have some concerns about the wall loss correction methods used in this study. For the lower-bound estimate of SOA formed the authors use size-dependent wall loss rates previously determined in calibration experiments. I expect these wall loss rates to change over the course of long experiments as the chamber is slowly depleted due to instrument sampling. The calibration experiments were shorter and used a smaller number of instruments than the experiments in this study; therefore, the decrease in chamber volume was smaller during the calibration experiments and may not be reflected in the size-dependent wall loss rates. It is somewhat reassuring that the wall-loss corrected OA mass stays constant after the lights are turned off (Figure 7), but the experiment in Figure 7 was only 20 hours long. The authors should address the extent to which the chamber was depleted in the 36 hour experiment discussed in this manuscript compared to the calibration experiments. It would also be appropriate to note whether the wall-loss corrected SOA mass was constant at the end of the 36 hour experiment. The upper-bound estimate is based on organic/sulfate ratios and makes the assumptions that 1) wall-deposited particles participate in gas-particle partitioning as if they were in suspension and 2) particles are internally mixed and therefore organics and sulfate have the same wall-loss rates.

The second assumption may not hold if the organic vapors condense onto the surface area of the inorganic seeds, in which case the organic size distribution will be shifted to a smaller size and (at the size ranges discussed here), the organics are expected to have a higher wall-loss rate than sulfate. This could explain the modest decrease in organics/sulfate after the lights are turned off (Fig. 7). Assuming that the authors collected pToF data with the AMS, it would be appropriate to examine the size distributions of organics and sulfate to evaluate whether they are perfectly internally mixed. The authors could also calculate size-dependent wall loss rates for organics and sul-

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fate separately. It would be interesting to see some analysis on how much these assumptions and their potential flaws might affect both upper and lower bound estimates. There is no perfect wall loss correction (esp. not for 36 hour experiments), but a bit more discussion would be appropriate.

Minor comments

p. 24975, line 26: sentence starting with "When comparing...". I am a bit confused about what the authors are trying to say here. The relative ionization efficiency (RIE) used in the AMS is relative to nitrate, and it should be different for organic and sulfate mass concentrations (1.4 and 1.2, respectively)

p. 24978, line 9: It would be appropriate to comment on potential changes in organic density with aging of the OA and how this would affect their results. Kuwata et al. (Harvard University) have developed a correlation between organic density and elemental ratios (O:C and H:C).

p.24979, line 1: I wonder why the authors used UMR AMS data for the total organic and sulfate concentrations since HR analysis was performed (O:C ratios are available). It would be appropriate to include a comment on how the sulfate concentrations from HR and UMR analysis of the AMS data compare.

p. 24980, paragraph starting on line 13. The different correlation of f44 and O:C in this study compared to the studies of Lambe et al. (2011) and Aiken et al (2008) is interesting. I find the mass loading to be an unlikely explanation since the loading in this study is more similar to the Mexico City study than the loading in the Lambe et al. experiments. Different AMSs measuring side-by-side can sometimes obtain different organic mass spectra. The authors should comment on whether the observed difference could be due to specifics of the instrument or data analysis. How much confidence do they have in the applicability to these experiments of the calibration factor (0.75) applied to O:C ratios obtained from AMS data? Have other studies using this AMS been able to reproduce the Aiken et al. correlations? A figure showing the mentioned correlations (Aiken et al. and this study) would be useful for visualizing differences.

p. 24983, line 24. While the substantial decrease does not exist anymore, there still is a decrease in organics/sulfate which should probably not be overlooked. See major comment above.

Figure 6. If I understood correctly, the authors consider two potential ways in which vapors can be “lost” to the walls: 1. condensation onto wall-deposited particles (this is captured in the upper-bound estimate of SOA formed) and 2. condensation onto the “clean” chamber walls. The figure illustrates only 2. but both of these vapor losses should probably be reflected in the model and the figure.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 24969, 2011.