**Atmospheric
Chemistry
and Physics
Discussions**

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

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We thank the reviewer for helpful comments. Please see responses below.

Major comment: part 1

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.

Response to major comment: part 1

The inferred wall loss rates in the experiments reported in this manuscript are based on calibration experiments performed approximately three weeks prior to the initial aging experiment and using the same methods as those reported in the references cited. Lines 18-23 on page 24977 have been rewritten as: "For each size bin i at each time step j the number distribution deposited to the wall, $n_{w,ij}$ is calculated using size-dependent wall loss rates, β_i:

$$n_{w,ij} = n_{s,ij} \exp\left(\beta_i \Delta t\right) \tag{1}$$

where $n_{s,ij}$ is the suspended particle number distribution in size bin i at time step j, and Δt is the difference between time step j and time step $j + 1$. Wall loss rates were determined from calibration experiments performed prior to the start of the aging experiments (methods detailed in Keywood et al. (2004); Ng et al., 2007)."

To address the time-dependence of particle wall loss rates during long experiments, the following paragraphs have been added to the manuscript after line 9 on p 24978.

"Throughout an experiment, the volume of the chamber decreases due to sampling, but the surface area of the walls remains the same. It is possible that the increasing surface-area-to-volume ratio will increase the particle wall loss rates. The duration of

a typical wall loss experiment is 18-24 h, shorter than that of the longest aging experiments. The aging experiments were designed to minimize the amount of air sampled from the chamber. Although more instruments sample from the chamber during an aging experiment than during a wall loss calibration experiment, the volume of air removed during an aging experiment is comparable to that of a wall loss calibration experiment (Table 1).

To confirm that wall loss rates do not vary significantly as chamber volume decreases, an additional wall loss calibration experiment was performed in each chamber. These calibration experiments were conducted following the same protocols as a typical wall loss calibration; however, before AS seed aerosol was injected, approximately 8 m^3 of air was removed from the chambers to simulate conditions found at the end of an 18 h experiment. The wall loss rates determined from these low-volume experiments were within the range of wall loss rates observed in the chambers since they were installed in 2009 (Fig. 1). Therefore, time-dependence of the wall loss rate constants was assumed to be negligible during these aging experiments."

Table 1 now includes the total volume of air removed from the chambers during wall loss calibration experiments (6.14 m^3), 18 h aging experiments (7.92 m^3), 24 h aging experiments (3.60 m^3), 30 h aging experiments (3.63 m^3), and 36 h aging experiments (3.66 m^3). Figure 1 has been added to the manuscript. It shows the wall loss rates as a function of D_p for both chambers from calibration experiments performed September 2009 to August 2011.

Major comment: part 2

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 sulfate 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.

Response to major comment: part 2

PToF data were not recorded for these experiments, and we are unable to confirm that the decrease in SOA mass observed with the upper bound wall loss case is a result of size-dependent organic-to-sulfate ratios. To evaluate the effects of a size-dependent organic-to-sulfate ratios and size-dependent particle wall loss rates on the magnitude of organic aerosol wall loss and subsequent wall loss corrections for the upper bound case, a simulation was carried out to model the wall loss of a particle number distribution for 3 different organic and sulfate mass distributions. A description of the simulation and its results has been added to the manuscript in a new section following Sect. 3.3.

Comment 1

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).

Response 1

The sentence has been changed to read, "A relative ionization intensity of 1.4 was applied to organic ion signals."

Comment 2

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).

Response 2

The following sentence has been added on p 24978 line 9, "It is possible that ρ_{org} changes as particle age increases, but it was assumed to be constant for the present study, which is consistent with the findings of Qi et al. (2010)." We are aware of the study by Kuwata et al. from conference presentations, but, to the best of our knowledge, it has not been published yet, so we are unable to compare to their data at this time. Determining changes in particle density with aging was not a principal goal of the present study, and analysis of the effects of particle aging on organic density is beyond the scope of this study.

Comment 3

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.

Response 3

The organic-to-sulfate ratio from UMR and HR data are in very good agreement (less than 5% difference between UMR and HR) during all but the initial growth period during the first two hours of the experiment. Organic ions at m/z 48 and 64 contribute to less than 1% of the total ion signal at each m/z. The UMR V-mode organic-to-sulfate ratio was used because of its relative ease of calculation compared to the HR V-mode organic-to-sulfate ratio. The following sentences have been added after the sentence ending on p 24979, line 2: "High-resolution analysis of the sulfate ions at m/z 48 and 64 showed less than 1% contribution of organic signal to the total ion signal; therefore, organic contribution to the unit mass resolution sulfate signal was negligible. Differences in the organic-to-sulfate ratio, r_{OS}, between unit mass resolution and high resolution data are less than 5%, except during the first 2 h of growth when they are more variable at lower organic loading."

Comment 4

p. 24980, paragraph starting on line 13. The different correlation of f_{44} 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.

Response 5

Chhabra et al. (2010) compared the trend of O:C vs f_{44} for SOA formed from a variety of anthropogenic and biogenic precursors to the correlation developed by Aiken et al. (2008). The results of this comparison are shown in Fig. 15 of Chhabra et al. Some of the systems reported showed a similar trend to the Mexico City data, but other systems deviated from the trend of the Mexico City data. SOA from aromatics (tolune and *m*-xylene) had a different trend than that of the Mexico City SOA. The authors present two reasons to explain this difference. The correlation developed by Aiken at al. best represents data in which a majority of the oxygen signal in the spectra comes from ions at m/z 44. If CO_2^+ contributes most of the oxygen signal in the spectra for SOA from a specific precursor, the trend of O:C vs f_{44} for SOA from that precursor matched that of the Mexico City data better than if most of the oxygen signal in the spectra occurred in other ions. Also, the Mexico City SOA is generated from a mix of precursors and represents a sum of individual precursor contributions. The chamber data represent the contribution from one specific precursor and may not follow the same trend as that of the ambient data. We have no reason to believe that the data analysis procedure was incorrect. As discussed in Chhabra et al. (2010; 2011), the O:C calibration factors from Aiken et al. are based on lab standards and may not be representative of SOA. Trying to determine a true SOA O:C calibration factor is beyond the scope of this work.

The following sentences have been inserted on p 24980 on line 20, "Using the same AMS instrument, Chhabra et al. (2010) found that the O:C and f_{44} of SOA from aromatics, isoprene, and glyoxal did not lie along the trendline reported in Aiken et al., but the O:C and f_{44} of SOA from α-pinene and naphthalene did. In general, if CO_2^+ contributed most of the oxygen signal in the spectra, then the O:C and f_{44} of the SOA more closely matched those predicted by the trendline from the Mexico City data."

The sentences on p 24980 lines 20-24 have been changed to read, "The range of f_{44} values observed by Lambe et al. is much larger than that in the present work, initial hydrocarbon loadings are higher, and OH exposure is much greater. Any of these

factors could contribute to the different correlations between O:C and f_{44}. The factor most likely to explain the discrepancy between the correlation in the present work and that in Lambe et al. is the difference in OH exposure between the present experiments and those of Lambe et al. At higher OH exposure, the SOA is likely to be more oxidized, and CO_2^+ is likely to be a major contributor to the oxygen signal in the spectra."

A figure has been added to the manuscript showing O:C vs f_{44} for SOA from *m*-xylene in the present work and Mexico City ambient aerosol and the O:C-f_{44} correlation for each of the data sets.

Comment 6

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.

Response 6

This comment has been addressed in the section added to the manuscript. See response to the major comment.

Comment 7

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.

Response 7

The figure has been revised to show condensation of A^g to particles deposited to the walls. The following sentences have been added to Appendix A after reaction (R23), "Neither gas-particle partitioning nor vapor-phase wall loss was included in the model because there is not sufficient information about either process to accurately represent it in the model. Vapor-phase wall loss is assumed to be minor (Fig. 10) and should not have a large effect on gas species concentrations."