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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

The composition of several experiments to one long term experiments relies on the assumption that the reproducibility is very good. The authors show indeed a good agreement between two 18h experiments. However, looking at the lower bound mass trace in Figure 2 I have some doubts on this. The 18h experiment starts already to decrease towards the end while after 22 hours mass concentration is slightly higher with a decreasing trend. This occurs again at hour 30. The measurements of the 24h

experiment are even missing. Why? Either the repeatability is not as good as stated or the wall loss correction does not work well. Regarding the latter I wonder if coagulation does not play a role when the wall loss rate of particle number concentration is determined.

Response to major comment: part 1

To explain how the DMA data were combined to calculate the lower bound wall loss correction, the following two paragraphs have been added on page 24978 after line 9.

“Calculating the lower bound wall loss corrected mass relies on having a continuous number distributions, which were not available for the 24-h, 30-h, and 36-h experiments. To obtain a continuous number distribution, the number distributions for all experiments were combined. The DMA sampling schedule was designed to allow a 2-h overlap period between shorter and longer experiments (i.e. sampling for the 24-h experiment began at 16 h, 2 h prior to the endpoint of the 18-h experiment) to facilitate the comparison of data between shorter and longer experiments. The number distributions from each experiment were combined sequentially. During periods of overlap between two experiments, a weighted average of the number distribution in each size bin was taken giving higher weight to the shorter experiment at the beginning of the overlap period and higher weight to the longer experiment at the end of the overlap period.

Both the number distribution of the seed particles and the initial concentration of *m*-xylene affect the size distribution of the aerosol. In the 24-h experiment, the seed volume was lower than that for the other AS seed experiments (Table 2). Assuming that the SOA produced in this experiment was comparable to that in the other experiments, the suspended particle volume would be lower than that of the other AS seed experiments, and the number distribution would be too small to combine with those of the other AS experiments to obtain a continuous number distribution. Without the data from the 24 h experiment, no number distribution data were available between hours 18 and 22. Number distributions during those 4 h were interpolated from the 18- and 30-h experiments by fitting an exponential function to the number distribution in each size bin during hours 16-18 of the 18-h experiment and hours 22-24 of the 30-h experiment and using the function to interpolate a number distribution at 4-min increments."

Table 2 has been updated to include the initial conditions for all of the experiments reported in the manuscript.

To clarify that data have been omitted and to explain the variation in the lower bound wall loss corrected mass concentration after lights off, the sentence on page 24979 lines 15-17 has been changed to read, "The lower bound ΔM_o and *m*-xylene data are a compilation of the 18-, 30-, and 36-h AS seed experiments (the 24-h experiment was omitted as noted earlier due to low seed particle volume), but the upper bound ΔM_o data are from only the 36-h experiment because continuous data were available. The variation in the lower bound wall loss corrected mass concentration after peak growth is likely due to differences in number distributions during the 18-, 30-, and 36-h experiments."

During wall loss experiments, the shortest coagulation timescale is > 20 h. Particles most likely to coagulate are 7-8 nm particles with 100-120 nm particles. Coagulation is expected to have minimal influence on wall loss rate calculations from calibration experiments.

Major comment: part 2

Now, it seems from Figure 2 that individual experiments show particle mass loss due to aging while the composed mass trace does not. Another issue with this is that the higher bound mass trace implies a mass loss while the lower bound estimate does not. However, most of the discussion and conclusion is on the mass loss of the aerosol as observed from the upper bound approximation. Somehow the authors assume that this

is the reality. This deserves some discussion. An implication of this is that the lower bound limit can become higher than the upper bound limit over a long time.

Response to major comment: part 2

Please see response to the major comment from Referee 2.

Major comment: part 3

If evaporation makes up almost 30% of aerosol mass (in Figure 1 mass decreases from 30 to 20 μg/m^3) I would expect to see that also in the size distribution. Figure 5 bottom panel shows a constant maximum diameter. I agree with the authors that evaporation and wall loss effects can have opposing effects on the maximum but not on the size distribution (page 24983 line 18). I would expect a clear narrowing of the size distribution from both sides. Taking the maximum diameter might not be the appropriate parameter to look at evaporation effects.

Response to major comment: part 3

The following sentences have been added on page 24983 on line 19. "It is also possible that the upper bound wall loss correction over-predicts the amount of evaporation occurring (see Sect. 3.4). In this case, the D_p at the size distribution maximum would only increase slightly toward the 200-300 nm minimum in wall loss rate."

Size distribution peak width at half height is another way to monitor the shape of the size distribution. Both wall loss and evaporation are expected to cause a narrowing of the peak width; therefore, evaporation and wall loss would not be distinguishable by monitoring peak width at half height alone.

Comment 1

Page 24980 line 8: The high O:C ratios in the beginning of the experiment seem to have a large scatter. The 30h and 36h experiment do not show these high O:C ratios in the beginning. Why? How reliable are these high numbers?

Response 1

The O:C data were reported once the V-mode organic mass concentration was at least 3 times greater than its background mass concentration; however, O:C was calculated using data taken with the AMS sampling in W-mode. Because W-mode has a lower sensitivity than V-mode, the O:C data have now been reported once W-mode organic mass concentration was at least 3 times greater than its background concentration. In the 18- and 24-h experiments, O:C decreases during the first 5 h of SOA growth. This decreasing trend is less evident in the 30- and 36-h experiments. For all the present aging experiments, O:C does not begin increasing until after 5 h of irradiation. The decreasing trend may not be as prevalent in the 36-h experiment as that in the other experiments because the overall W-mode sensitivity of the AMS was lower during that experiment than during the other aging experiments. The O:C measured with the AMS in V-mode decreases during the first 5 h of irradiation for all 5 of the aging experiments.

The sentences, “A prominent feature of the SOA formed in this system is that formed SOA initially has an O:C ratio of 0.7. Over the first 5 h of irradiation and SOA formation, O:C decreases to 0.6. After 5 h, O:C gradually increases at an average rate of 0.0019 h^{-1} for the remainder of the irradiation period.” have been rewritten as, “O:C decreases during the first 5 h of irradiation in all but the 36-h experiment. During the 36-h experiment, the sensitivity of the AMS sampling in W-mode was lower than that in the other aging experiments, which hindered the detection of initially-formed SOA. The O:C calculated using V-mode data (not shown) increases during the first 5 h of irradiation for all 5 of the aging experiments. The dominant trend in O:C begins after 5 h. After this time, O:C gradually increases at an average rate of 0.0019 h^{-1} for the remainder of the irradiation period.”

Comment 2

Page 24981 line 17: The statement “the total amount of each ion” relating to Figure 5 top panel is wrong. What is shown in Figure 5 is a relative normalized value.

Response 2

Please see response to Comment 4 of Referee 1.

Comment 3

Page 24983 line 25: Why does the lower bound mass still increase after lights off?

Response 3

The sentence “No decrease in ΔM_o for the lower bound limit is observed” on page 25983 line 25 has been replaced with, “The lower bound ΔM_o increases after lights are turned off to result in a 5% change in mass after 8 h. This increase could be the result of uncertainty induced by the wall loss correction or condensation of vapors as the chamber cooled after irradiation stopped from 24° C to 19° C during hours 12.4 to 16. The latter process is not observed in the upper bound ΔM_o, but condensation could be masked by uncertainty in the wall loss correction method, discussed in Sect. 3.4. Despite the potential uncertainties of the wall loss correction and the cooling of the chamber, the decrease observed in the lower bound ΔM_o in the 36-h aging experiment is not observed after irradiation ceases.

Comment 4

Page 24984 line 2ff: It states “After irradiation stops, no change in the amount and composition of the particles is observed”. I agree that the changes are much lower but there still seem to be some changes. f_{43} and f_{44} seem to evolve slowly and the *upper bound mass estimate slightly decreases. Why is the organic to sulfate ratio decreasing? Has this to do with the fact that organics condense faster on smaller particles, thus r_{OS} is higher, but are lost at a higher rate to the walls? How large is such an effect?*

Response 4

The first half of the sentence has been rewritten to read, “After irradiation stops, the rate of change in the amount and composition of the particles decreases substantially. . . .” For the responses to the remaining questions, please refer to the response to the major comment from Referee 2.

Comment 5

Page 24984 line 18ff: please indicate in the text where the notation of compounds and rate constants can be found.

Response 5

Added a reference to Table 3.

Comment 6

Page 24985 line 20 and Figure 9: To me the time trends shown in the top and middle panel seem to be similar. Both start to increase immediately. Why should the middle panel present a second-generation oxidation product except that the m/z fits with a possible reaction product?

Response 6

The timing of the peak of the signal at m/z 223 indicates that it could be a second-generation product. The following sentence has been added on line 24 on page 24985: “The photochemical model predicts the peak of the first generation product concentrations to occur about an hour before that of the second generation product concentrations, and the time difference between the peak of the CIMS signals at m/z 207 and m/z 223 is consistent with the model output.”

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