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Atmospheric Measurement Techniques Discussions

Interactive comment on "Particle Wall-loss Correction Methods in Smog Chamber Experiments" *by* N. Wang et al.

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Wang et al. presented a study that evaluated the performance of different particle wall loss correction methods for aging experiments of α-pinene ozonolysis products. This paper may potentially be useful to the SOA chamber community. However, there are portions of the manuscript that are vague and confusing, and they need to be addressed before it can be considered for publication.

We address the various comments of the reviewer below. Our responses (regular font) and corresponding changes in the paper follow each comment (in italics).

(1) *Page 5, line 141: How many particle wall loss experiments are typically performed*

during the year? How reproducible are these particle wall loss rates? It would be useful to show the rates obtained during these (1-year worth of) experiments in the SI.

The annual number of wall loss experiments has been variable. During 2016 there were around 15 experiments. After their potential variability became clear due to the maintenance of the simulation chamber, we perform them every week. The reproducibility is clearly related to the status of the chamber. When the chamber is in its disturbed state loss rates can vary by more than a factor of 5 and they can be quite high. When the chamber is in its undisturbed state the loss rates are a lot smaller and they can vary by 0.05 h^{-1} or so. The 4 curves shown in Fig. 3 are representative of the range. We have added some text in the paper to discuss this variability.

(2) *Figure 1: Why are the measured k's only shown for particles of diameters < 400 nm and < 800 nm for the 12 m^3 and 1.5 m^3 reactors? What about the particles with larger diameters? Were those measured? If not, why not?*

The particle loss rate constants for a given size can be measured reliably only when there are enough particles of this size available in the system. In the experiments shown, the produced ammonium sulfate particle size distribution included few larger particles. As a result, the k's at bigger particle sizes had high uncertainty associated with them due to lack of particles, and were thus excluded from the figure. This is now explained in the manuscript.

(3) *Page 8, line 226: I am inferring from Fig 1 that if k_a is larger than k_c, coagulation is a significant particle loss process. Is this correct? If yes, this should be stated explicitly in the main text. Currently, there is little explanation in the text of what differences between k_a and k_c shown in Fig. 1 means.*

The reviewer is correct that coagulation is a significant particle loss process for the size range where k_a is larger than k_c. We made corresponding changes in Section 4.1 of

the revised manuscript to explicitly state the above fact and address the differences between k_a and k_c.

(4) *Page 8, line 232: It would be useful to show in the SI how the particle wall loss rate constants look like after correcting for coagulation.*

Figure 1 depicts the effect of the coagulation correction. A reference to that figure and some additional discussion have been added at this point.

(5) *Page 8, line 234: "The uncertainty of ... is significantly higher ..." How much higher? Please give a number.*

We now state that the uncertainty increases from approximately 10 to 50 percent.

(6) *Page 8, line 236: "This is due to ... versus the linear regression that uses the measured." It is unclear which linear regression fit the author referring to. Is it the linear regression fit to each particle size bin or the linear regression fit of the measured k_a's?*

We refer to the linear regression fit of the logarithm of the concentration of the particles in each size bin. This is now clarified in the text.

(7) *Figure 2: Why doesn't k_c correct for the effect of particle wall loss on the number concentration well? This was not explained in the main text.*

k_c, being the coagulation-corrected particle wall-loss rate constant, intrinsically excludes the impact of coagulation on particle number concentration. Since coagulation reduces particle number (but conserves mass), k_c-corrected particle number concentration is lower than the k_a-corrected one, with the difference attributed to the coagulation rate. The corresponding explanation has been added to the paper.

(8) *Page 9, line 243: Why weren't the k_a's for D_p < 50 nm measured? If they were measured, there would be no need to back extrapolate the data.*

The reason for extrapolation of k_a's for D_p < 50 nm is that the measured k_a's were extremely uncertain due to lack of particles at those small sizes and thus could not be used. This is now explained in the revised paper.

(9) *Page 9, line 249: "As a result, the coagulation effect is almost an order of magnitude higher than the average ..." What do you mean by the "coagulation effect"? Are you referring to the rate constants? Please clarify.*

We have rewritten the corresponding sentence which refers to the difference between k_a and k_c due to coagulation.

(10) *Page 9, line 259: "Our results are consistent with their low seed ..." Which results are you referring to? Your SOA mass yields? Your observation that coagulation plays a minor role in some of your experiments? Please clarify.*

We have deleted this rather confusing sentence.

(11) *Page 9, line 262: What were the particle number concentrations used in these ammonium sulfate-only experiments? Were they somewhat similar? Also, the uncertainties are missing from the figure.*

The particle number concentrations used in these experiments varied from approximately 10,000 to 40,000 cm^{-3}. The uncertainties of the k_c curves are shown in Figure S1. We made the corresponding changes in the revised manuscript to direct the readers to Figure S1 for the uncertainties.

(12) *Page 10, line 283: How did you determine when condensation/evaporation was minimal in your experiments? By using your SMPS data? Or the AMS data?*

We used both the SMPS and the AMS measurements. This is now mentioned in the text.

(13) *Page 10, line 285 to 293: The authors claimed that k_a and k_c are almost the same except for particles smaller than 100 nm. Can the observed differences at the smaller particle sizes really explain the differences in the size-independent loss rate constant? A more detailed analysis should be presented.*

There are two different issues here that should not be confused. First there is the difference between the two rate loss constants which increases for smaller particles. Then there is the size dependence of either constant. The errors introduced during the use of a size-independent rate constant are mainly affected by the size dependence of the "true" rate constant over the size range covered by the aerosol size distribution. We have added a more detailed discussion of this point.

(14) *Figure 4: Was the SMPS only scanned up to 300 nm? If yes, why was this the case? It looks like that the entire volume/number concentration distribution was not captured. This may affect the accurate determination of SOA mass concentrations in Fig. 5.*

The SMPS measured up to 700 nm for this experiment. Due to the large uncertainty of kc at diameters above 300 nm, we assumed a constant kc value for the larger sizes. This is a reasonable assumption because kc remains relatively constant from 300-500 nm based on our measurements (Fig. 3) when the chamber is undisturbed. Please note that most of the SOA mass in this experiment was in particles smaller than 300 nm (Fig. 4b). Thus assuming a constant wall loss rate constant for particles larger than 300 nm should have only a small effect on the corrected SOA mass concentration. A brief discussion of this point has been added to the paper.

(15) *Page 10, line 295 and Figure 5: What is the main conclusion of section 4.3?*

Should the size-independent method be used given that their corrected SOA mass concentrations are so different?

We conclude the corrected SOA mass concentration can vary by 20-30 percent depending on which wall-loss rate constants are used. We recommend using the size-dependent wall loss rate constants for the correction. However, when the chamber is undisturbed and the duration of the experiment is a couple of hours, using the size-independent wall loss rate constant derived from the initial 4-hour seed wall-loss period can give relatively accurate results (errors of 5 percent or less). We have rewritten part of this paragraph to make our conclusions clear.

(16) *Page 11 line 315: "Particles of smaller sizes with larger organic to sulfate ratios. . ." Loza et al. (ACP 2012) previously discussed in detail the effect of size dependence wall loss on the organic to sulfate ratio. Thus, that paper should be cited.*

We have added the citation to the work of Loza et al. (2012) at this point.

(17) *Section 4.5: When were the particle wall loss correction applied? Just before the start of SOA formation (time = 0 min) or when the ammonium sulfate seed was first injected into the chamber?*

The particle wall loss correction was applied when the ammonium sulfate seed was first injected into the chamber, as depicted in Figure 8a. This is now clarified in the paper.

(18) *Page 14, line 420: It was recommended that metal gloves be used if it was absolute necessary to touch the chamber walls. Was this recommendation tested? Did using metals gloves really resulted in less electrostatic forces in the chamber and thus smaller differences in the measured k's? If yes, the data should be shown to back up this recommendation.*

We have rephrased this sentence given that we have only anecdotal evidence to support this recommendation. We now state that “other practices like use of metal gloves can help reduce the build-up of static electricity on the chamber walls.

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