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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurement of ambient aerosol hydration state at Great Smoky Mountains National Park in the Southeastern United States" *by* N. F. Taylor et al.

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We want to thank both referees for their careful consideration of the manuscript. We have tried to reciprocate that attention in our response. As all parties here doubtlessly understand, this manuscript is the product of much sweat. Where we disagree with the referees, please sympathize with the earnestness of our responses. We have done our best to clearly describe the rationale for these disagreements. If indeed we are wrong, please help us to understand the flaws in our reasoning.

We respond to the referee's comments in sequence. Please also find the sub-

sequent, revised versions of Figs. 6-9.

Response to Anonymous Referee 1

1.1

"It seems, however, that the characterization of more and less hydrated states is somewhat confusing. In some of the discussion there seems to be an implication that the particles passing though the AS-TDMA are of one type of particle as opposed to an ensemble of particles, some that do not show hysteretic behavior, some that at some time in their past history have deliquesced, and some that have not. For instance, see on page 9, line 289, the sentence ". . .that the particle is hysteretic and. . ." The AS-TDMA does not measure particle characteristics but rather characteristics of ensembles of particles with similar characteristics. This may seem minor but is confusing to the reader when trying to understand how the instrument was ultimately used under ambient conditions. In that context, I think Figure 2 and the associated discussion could be modified, discussing an ensemble of particles with these three characteristics and relating it to the size distributions shown in the lower right. Remove the size distribution graphs directly adjacent to the D/Do curves – it seems that this "ideal" aerosol never occurs, or if the authors chose to keep the curves, it should be made clear that they are associated with a distribution of particles with the same hysteretic characteristics."

General Response

This point is well taken. The discussion of instrumentation and operation has been altered to emphasize that TDMA results deal in particulate ensembles. Further, we

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have added an explicit description of this on line 282. For discussion of the distributed response depicted in Figure 2, please see line 243.

Specific Changes

line 148, “particles” changed to “an ensemble of particles”

line 151, “an aerosol” changed to “a particle ensemble”

line 235, “This aerosol has” to “The particles in this ensemble have”

line 244, “a uniform aerosol” to “an ensemble of uniform, internally mixed particles”

lines 282-286, inserted, “Finally, if the aerosol was externally mixed, the resultant size distributions from this and the other processes would contain, superimposed, the responses of the different factions in the aerosol. For example, the results in the lower left depict an external mixture with several distinct populations."

line 306, “particles” changed to “aerosols”

1.2

"Figure 1 can be eliminated. The discussion on this page can be referred to Figure 2, which shows the same information."

General Response

The purpose of Figure 1 is didactic. Figure 2 is not identical as it depicts the hydration characteristics of an aerosol with the less familiar feature of partial hydration of the less hydrated state. This is an important part of our results, but is an added confusion at the early stage at which Fig. 1 is referenced. I assume that people recognize

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the terminology of “meta-stably hydrated” and “thermodynamically stable, crystalline” making this a logical bridge to the concepts of “more-“ and “ less-hydrated states”; however, I cannot reference Fig. 2 with these terms. Thus, the more common example of ammonium sulfate is included as a point of contact with common knowledge.

1.3

> *“Estimating dissolution RH using the AIM model, which only applies to inorganics when organics are present and when most of the summer aerosol did not even show hysteretic effects, seems to be inappropriate at best. Furthermore, using ammonium data from the IMPROVE network will result in a substantial underestimation of true ambient ammonium concentration. It has been shown that, especially in the warm summer months, much of the ammonium collected on a nylon filter will volatilize. Because of this volatilization issue, ammonium measurements have been discontinued in the IMPROVE program. An underestimation of ammonium will result in an estimated dissolution RH that is substantially lower than what it would be for the ambient aerosol. Therefore any discussion and model calculations using IMPROVE ammonium should be removed from the manuscript.”*

General Response

The primary purpose of the AIM model calculations in this paper is to support the AS-TDMA results. Here, we only want to indicate that the seasonal difference in composition is likely part of the cause of seasonal differences in AS-TDMA results. We severally and emphatically stress that filter based measurements are not ideal for this purpose, and that they are used because they were the only composition data available. The AIM model is employed as a simple method to translate composition into a quantity relevant to our measurements. It is only intended to aid in interpreting the data. Our justification for not treating organics as given in the paper (see p. 16,

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line 544) is valid because we only intend the AIM results as a simple aid.
Those caveats notwithstanding, we found a persistent correlation between our AS-TDMA results and the AIM model results. This is shown in Fig. 13. This correlation is a final justification for this treatment: The AIM model applied to filter based composition measurements does anticipate the hydration characteristics of the aerosol. This supports our AS-TDMA measurements and nicely broadens the context of the paper.

Again, a primary emphasis in our results is the seasonal contrast between the two reported study periods. We support the seasonal contrast in our result with seasonal contrast in particulate composition and meteorological conditions. For the summer, it is exactly our goal to show that infrequent detection of hysteresis is well anticipated by predictions of low dissolution RH in conjunction with generally high ambient RH. This seems to us a perfectly appropriate comparison.

For justification of the use of the IMPROVE results in this context we refer to the text of the 2nd ed. of Atmospheric Chemistry and Physics by Seinfeld and Pandis, section 10.4.4. (p. 478-83; paperback). Our argument hinges on the following two points:

1. The vast majority of ammonium volatilization is associated with ammonium nitrate. The volatilities of all ammonium/sulfate compounds are marginal.

2. Ammonium nitrate does not partition readily to any sulfate particulates that are acidic.

Thus, we contend that the summer period at GRSM does not suffer from ammonium volatilization because little ammonium nitrate exists in a milieu dominated by acidic sulfate species, and ammonium associated with sulfate is not volatile except in extreme conditions.

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The winter filter measurements are more likely problematic. In that period, the sulfate is totally neutralized and ammonium nitrate can partition to the particles. The addition of ammonium nitrate depresses the dissolution RH, but not drastically. In equal parts (molar) with ammonium sulfate, the reduction versus pure ammonium sulfate is approximately 6% RH. Thus, we believe the likely error introduced by volatilization is a small overestimation of dissolution RH, rather than a substantial underestimation. This is much lower than the seasonal signal which is the major feature we want to portray.

Finally, we note that for a simple ammonium sulfate/ammonium nitrate aerosol, the loss of ammonium nitrate necessary to produce a 6% increase in deliquescence RH would decrease the size of an aerosol by $\sim$10%. We would expect that losses of this order would also appear in the unperturbed (originally hydrated or non-hysteretic aerosol in DF measurements, originally less-hydrated or non-hysteretic aerosol in EF measurements) portions of AS-TDMA results. However, while size reductions were occasionally detected in this fashion ($\sim$15% of measurements), losses of this magnitude were very rare indeed (<1%). 90% of the time, losses were less than 2.5%. This constrains our expectation of filter volatilization and our expectation of the impact of volatilization on AS-TDMA results.

In the manuscript, we have added a brief discussion of ammonium volatility both in this context and in the context of our instrument.

Specific Changes

lines 403-408, inserted, “Filter based measurements are also fraught with volatilization issues, especially of ammonium. However, the sensitivity of dissolution behavior predicted by AIM to the volatilization of ammonium is quite moderate. This claim is based on the supposition that the ammonium lost is associated with ni-

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trate and that the locally ubiquitous sulfate fraction of any aerosol particle containing ammonium nitrate is fully neutralized (Seinfeld and Pandis, 2006). Thus, it is expected that the winter dissolution estimations were only moderately, artificially high."

1.4

"Page 16, section 3.1.2: I believe this section, along with Figure 5, can be removed from the manuscript. The focus of the manuscript is on the AS-TDMA results, and section 3.1.2 adds very little to the main focus of the paper. Figure 5 merely shows an example scan that can be found in many other places in the literature. The deliquescence/efflorescence summary would be of interest if it represented the same scans or time periods associated with the AS-TDMA, which it apparently does not because of intermittent instrument issues."

General Response

This brief section was included to reinforce the AS-TDMA results and methodology. The AS-TDMA is a fairly new and unproved instrument. Thus, we are eager to show any ancillary validation of its results. We admit that the discussion in the paper does not strongly suggest this purpose and have made changes accordingly.

We have altered our wording in this section to emphasize that the deliquescence/efflorescence summary does indeed represent the winter measurements. We feel that this summary provides validation of the AS-TDMA results and have indicated a simple comparison in the added text.

The two growth curves are indeed rather generic but we feel that their inclusion is justified at three points: they illustrated the water amounts on which AS-TDMA

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measurements typically hinged at the GRSM site; they simply reminded readers of the RH scan operation of H-TDMA; and they at least illustrate the presence of both hysteretic and non-hysteretic behavior by means other than AS-TDMA measurements. Thus, they help reinforce AS-TDMA findings.

Specific Changes

lines 430-432, inserted, "Finally, the H-TDMA phase transitions compare well with the average winter deliquescence RH roughly indicated by the AS-TDMA results as shown in Fig. 12.

lines 422-423, inserted, "The two example scans are sufficiently typical and highlight the amount of water operative in AS-TDMA measurements."

1.5

> *"Figures 8 and 9 contain many data points that are overlaid on each other and can't really be differentiated. They add very little if anything to the main essence of the manuscript in that they only show data collected in two sampling periods. I suggest that these figures along with the associated discussion be removed from the manuscript."*

General Response

We grant that Fig. 8 and 9 are quite difficult to parse; therefore, we have taken several steps to simplify and clarify those depictions. It is our belief that the results shown in Figures 8 and 9 are very significant and interesting. The variation in hydration state over time is not something that has been explicitly measured or shown before. Further, these results give a better feel for the character of AS-TDMA results than any other

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presentation we include.

Specific Changes

Figures 8 and 9. The number of sizes depicted is reduced from 5 to 2. The format of the error bars is simplified and their footprint reduced.

Associated chart descriptions were changed.

1.6

"Figure 13 and associated discussion should be removed from the manuscript, especially in light of the error in the bulk IMPROVE ammonium measurements. Also, the AIM model does not account for organic/inorganic interactions, and therefore dissolution calculations using this model are not expected to be representative of typical ambient aerosols."

General Response

Again, we emphasize that the presence of clear features in Fig. 13 is at least partial justification for our use of the AIM model. It does not seem to us a poor first step.

Response to Anonymous Referee 2

2.1

"It would probably be better to split the manuscript into two, one dealing with the instrument and its characterization, the other concentrating on the results of the field campaign."

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General Response

This has been on the mind of several of the authors. In lieu of splitting the manuscript, we have attempted to mitigate the lengthiness by removing some of the measurement analysis discussions to an appendix. While wordiness remains an issue, we believe that this improves readability and flow.

Specific Changes

The majority of section 2.3 was converted into an appendix.

2.2

> *"Were any aerosol neutralizers used in the instrument? Their position should be indicated in the flow diagram (Fig.2.)."*

General Response

We agree that this should have been included in the instrument description. While neutralization is an essential part of TDMA systems (warranting its textual inclusion, certainly) we would rather leave it out of the schematic. This preference is mainly due to space constraints in an already cluttered graphic.

Specific Changes

lines 168-170, insert, "The ambient aerosol is sampled with a simple inlet and passes through a Po-210 based neutralizer before entering the first classifier. "

2.3

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"The output of the first DMA always contains multiple-charged particles. How were these multiple-charged particles accounted for when correlating modes measured at different RH (section 2.3.2)?"

General Response

The presence of multiply charged particles was not explicitly accounted for in the mode correlation, but I would minimize the effect that multiply charged particles have on our results. First, due to the normal ambient size distributions during these periods and the expected charge distribution, multiply charged particles will only be a significant issue (contribute more than 8% to the AS TDMA resultant size distribution) for the 100 nm size range. There, it occasionally will contribute 25% (more normally, $\sim$18%) of the distribution. This is significant. Of course, as with all TDMA type measurements, multiply charged particles only impact the results to the extent that there are differences between the characteristics of the singly- and doubly- charged particles. This condition indeed applies occasionally, but by no means consistently, for 100 nm (single) and $\sim$150 nm (double) populations.

Still, this is an unfortunate issue with this data set and we have added some discussion of the problem in the manuscript. It would be better to account for these multiply charged particles in the inversion routines; however, this requires at least concurrent knowledge of the ambient aerosol size distribution—a property not consistently available during these projects.

Specific Changes

Lines 1062-1074 (Appendix A.5), inserted, “At this stage, no attempt has been made to recover the effects of multiply charged particles in the AS-TDMA results. This is due primarily to unfortunately unavailable, necessary knowledge of the concurrent ambient size distribution; but, also to the non-triviality of developing the

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necessary procedures. Based on the limited ambient size data available, it is expected that multiply charged particles will very rarely contribute more than 8% to the resulting AS-TDMA size distributions, save for the 0.1μm ambient diameter measurements. At that size, the normal contribution is closer to 18%. This is significant, but note that multiply charged particles only blur "size-resolution" and are evident only when sharp transitions with size exist in the response to the inter-DMA process (i.e., when the lost "size resolution" becomes salient). In conclusion, it is possible, in principle, to retrieve these errors with data procedures; these have not yet been developed for the AS-TDMA; and this lack does not greatly undermine the value and use of this data set."

2.4

"The internal enclosure is said to have been maintained at 29C. Was this so also during winter? I am concerned about potential volatilization losses of ammonium nitrate and semi-volatile organics that could affect the observed particle size changes."

General Response

The enclosure was indeed kept around 29C. And it is likely that there would be some volatilization losses of particle mass. However, we do not expect that, in this environment, these will entirely disable the use of the AS-TDMA results. First, beyond a (hopefully) uniform shift in particle size for each process, these changes should not largely effect the hydration state measurements. This claim is based on the generally limited impact on the phase transition behavior of a dominantly ammonium sulfate of adding even soluble material (cf. discussion with referee 1 above concerning AIM dissolution predictions and the marginalization of the impact of organics given in the paper). A uniform shift in all three process measurements in a given measurement set is treated (along with shifts driven by RH) by our result processing routines (see

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section 2.3.4). Thus to first order, volatilization effects should be limited.

We do agree that this is not ideal. We may attempt to operate an entire instrument under external conditions in the future, though that would present other problems involving temperature heterogeneity. For now, we have added mention of the possibility of volatilization.

Specific Changes

lines 175-178, inserted, "This admits the possibility of some volatilization of compounds such as ammonium nitrate; yet, hopefully with limited impact on the results (c.f. section 3.1.1 for the impact of ammonium nitrate volatilization on hydration behavior and A.4 for the recovery of systematic mass loss)."

lines 403-408, inserted, "Filter based measurements are also fraught with volatilization issues, especially of ammonium. However, the sensitivity of dissolution behavior predicted by AIM to the volatilization of ammonium is quite moderate. This claim is based on the supposition that the ammonium lost is associated with nitrate and that the locally ubiquitous sulfate fraction of the initial aerosol is fully neutralized(Seinfeld and Pandis, 2006). Thus, it is expected that the winter dissolution estimations were only moderately, artificially high."

2.5

"The manuscript is missing some relevant citations. Martin et al. (2008) reported measurements of ambient aerosol hydration state using a similar, though differently implemented, approach . Work of Stanier et al. (2004), Khlystov et al. (2005) and Engelhart et al. (2011) on the water content and, thus, the hydration state of ambient aerosol should also be cited."

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General Response

We have added discussion of the DAASS in that part of the introduction that considers other instrumentation. The 1 x 3 TDMA used by Martin and Rosenoern at the SGP ARM site could, with only slight modification, retrieve hydration state. However, the experiment described in that paper does not well utilize this capability. The primary obstacle is the differential between the inlet and ambient RH for their measurements. During the day, the significantly cooler inlet temperature created a large positive perturbation of RH, obscuring the ambient hydration state by prematurely forcing deliquescence. While some attempt was made in that paper to retrieve this artifact, it irreparably removed knowledge of ambient hydration state when the aerosol experienced RH higher than the deliquescence RH before being size classified. In short, experiments reported were not run to extract hydration state, but to detect phase transitions. We have added reference to this technique, but in a way that glosses over the details and only suggests that instrument's promise.

Specific Changes

lines 76-88, inserted, "Other current approaches to measuring hydration state are the nephelometry based work of Rood et al. (1987; 1989), the 1x3 TDMA Martin et al. (2008) and Rosenoern et al. (2009), and the Dry-Ambient Aerosol Size Spectrometer (DAASS) (Engelhart et al., 2011; Khlystov et al., 2005; Stanier et al., 2004). From the high time resolution of nephelometry to the broad size range examined by the DAASS to the notable sensitivity of the 1x3 TDMA, each has various advantages. However, when considering the alternative hydration states resulting from hysteresis these approaches have less merit. The work of Rood et al. only positively indicates the presence of a more hydrated alternative state, while the DAASS does not treat hysteresis. Both could, with sufficient supporting measurements of hysteresis behavior or composition, more fully address alternative hydration states; but this is not inherent in their function. Further, though

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these instruments do in some fashion retrieve size dependence, it is not with the clarity, resolution, or ability to determine mixing characteristics available to TDMA based systems. Alternatively, the 1x3 TDMA has advantages of sensitivity as well as the capability to indicate hysteresis and the ambient hydration state. But this capability has yet to be exploited in field deployments.

In the remainder of the introduction, fairly extensive changes were made as necessary to accommodate this insertion.

2.6

"Figures 6 and 7: I do not think the color gradient as a function of size is needed here. It makes the picture more confusing and difficult to read. The minor tick labels are missing '.' before the numbers (should be '.9' or '0.9' instead of '9')."

General Response

We have implemented these suggestions.

2.7

"Figures 8 and 9: I suggest to remove the error bars. They represent the width of the mode, which does not really contribute to the story here, but obscure the midpoints considerably, making the figures very difficult to read."

General Response

In response to general concerns of readability, we have adjusted these figures. They now track 2 sizes, rather than all five. I have not removed the error bars, for a variety of reasons. While you are quite right that the information they provide is not generally

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interesting (though they do nicely indicate cases where two modes have merged to form one, see 12:00, 07 December 2007), they do help locate points partially obscured by other points, retain the vertical axis so important for time series, and add emphasis to minor modes. In lieu of removal, I have weakened their emphasis significantly.

Works Cited

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 21877, 2011.

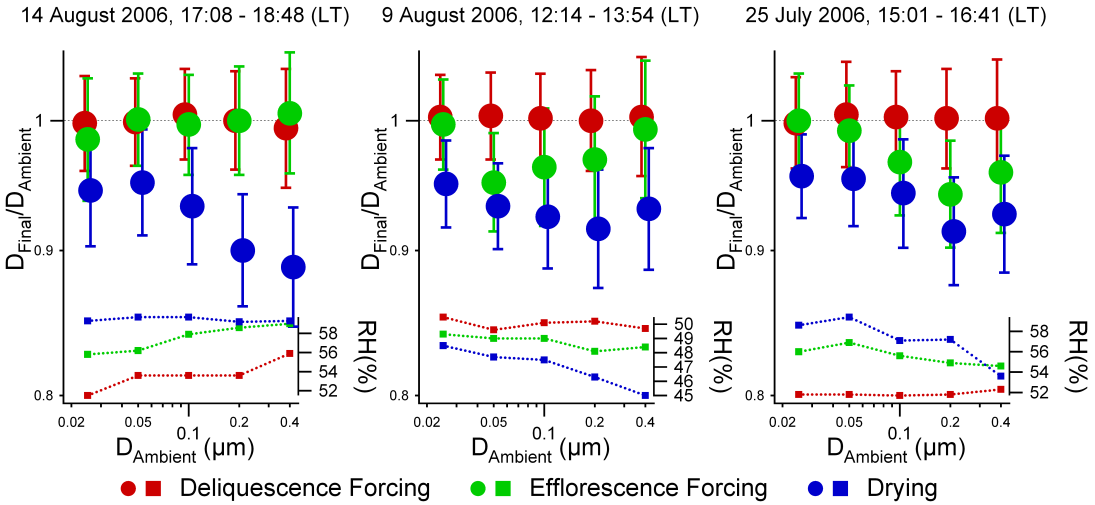

Fig. 1. Fig. 6 Revised

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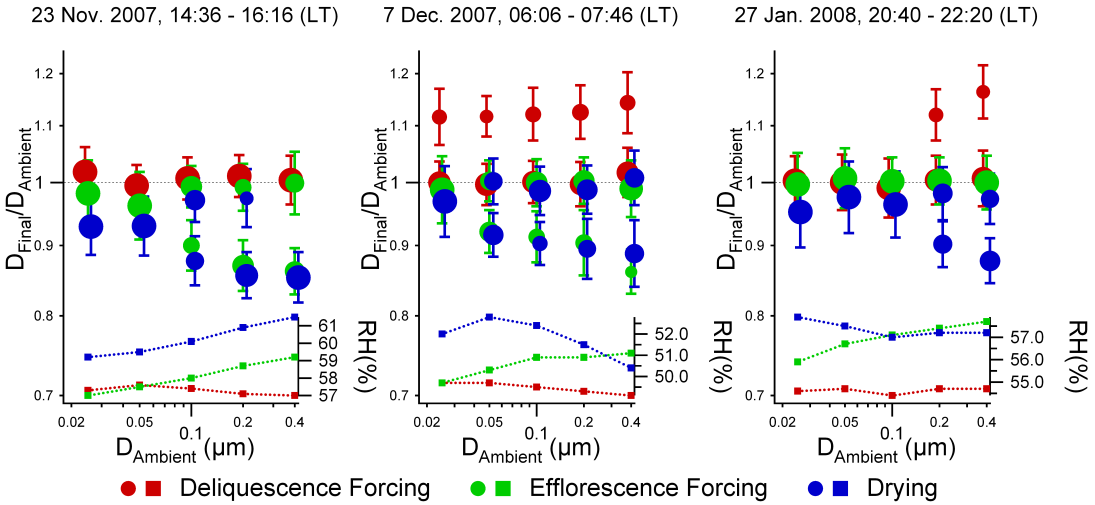

Fig. 2. Fig. 7 Revised

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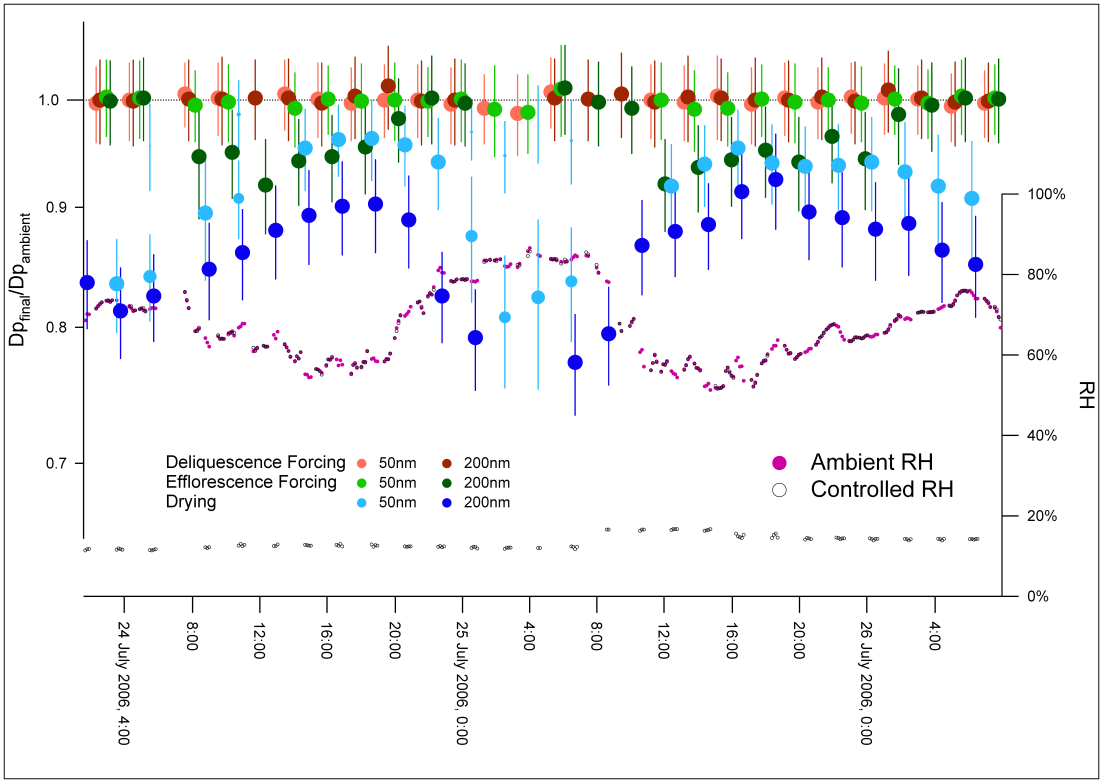

Fig. 3. Fig. 8 Revised

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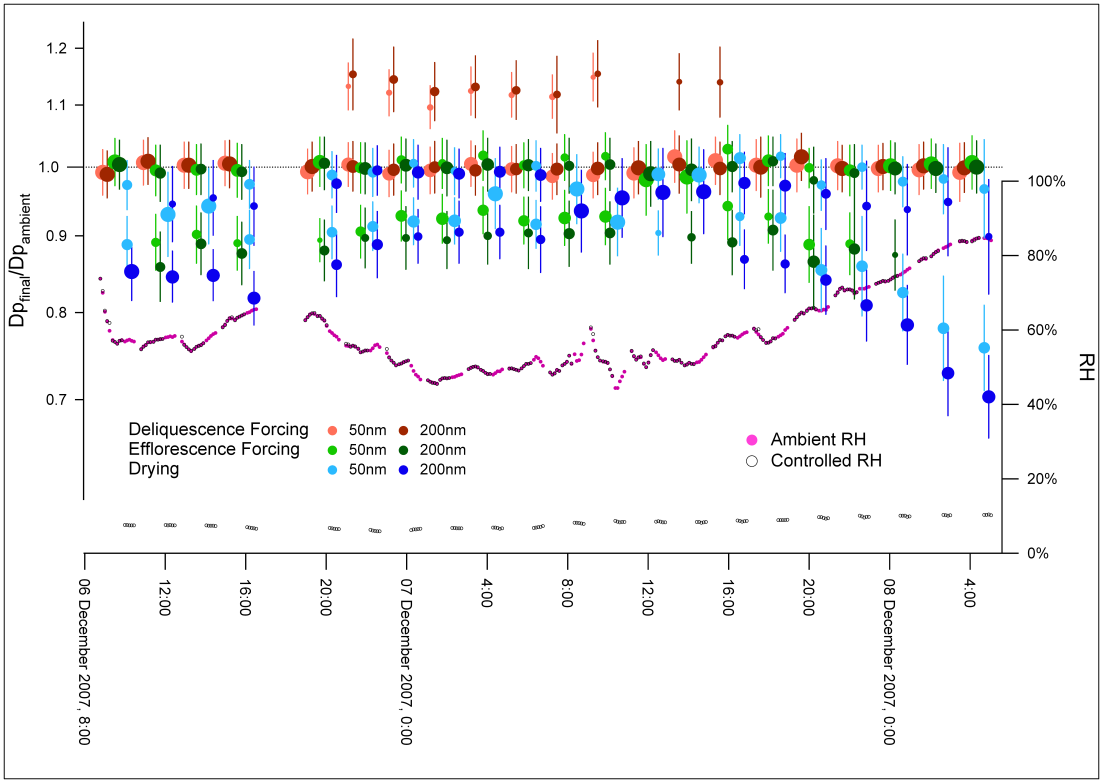

Fig. 4. Fig. 9 Revised

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Interactive Comment