Atmos. Chem. Phys. Discuss., 15, C12352–C12364, 2016
www.atmos-chem-phys-discuss.net/15/C12352/2016/

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Aerosol optical properties in the southeastern United States in summer – Part 1: Hygroscopic growth" *by* C. A. Brock et al.

C. A. Brock et al.

charles.a.brock@noaa.gov

Received and published: 12 February 2016

Response to Reviewer 2 Manuscript Number: ACP-2015-670 Manuscript Title: Aerosol optical properties in the southeastern United States in summer – Part 1: Hygroscopic growth

The discussion below includes the complete text from the reviewer, along with our responses and corresponding changes made to the revised manuscript . The authors thank the reviewer for useful comments that have improved the manuscript.

Comment: Brock et al. use airborne profiles of aerosol properties performed in the

southeastern United States to investigate the hygroscopic effect of aerosol particles on their extinction coefficient at three distinct relative humidities (RH). A new parametrisation is presented that is found to more adequately describe the observations than a different single parameter equation (γ-equation).

Although I have no doubts as to the high quality and scientific significance of the presented data, I see some major shortcomings in the analysis and the following interpretation. First of all, the paper uses airborne profiles of measured optical extinction enhancement factors (plus size distribution and composition measurements) but no profiles or interpretation of these are shown (in contrast to the title of the presented manuscript). This could be due to the fact that these will be shown in a companion paper. However, it is not acceptable that the data selection criteria that lead to the presented results are not accessible for the review process (quote from page 25699, line 20: "Part 2 also contains details of the selection of data for the analysis of both papers ...").

Secondly, the proposed parametrization is based on measurements at one dry and two elevated relative humidities only, which is an understandable and necessary compromise for airborne measurements. However, I doubt that three values are sufficient to propose a new and improved parametrization bearing in mind that many aerosol types show hysteresis effects which can not be described by a simple γ-fit. Due to the limited number of elevated RH measurements it is important that the authors present and discuss the (hygroscopic) calibration of their instrument with nebulized salts prior to each campaign or flight.

The paper would be substantially improved by

(a) more focused discussion of the actual profile measurements of the extinction enhancement, its vertical and spatial variation, its link to chemical composition and air mass origin (as the manuscript title also implies); and

(b) less focus on the parametrization of a three point measurement. There are further detailed comments given below (in arbitrary order) that should be adequately addressed before this manuscript can be published in ACP. It is for these reasons that I recommend major revisions.

Response: In response to these comments, we have made substantial changes to the content and structure of the manuscript, as requested. A PDF of the revised manuscript with major changes highlighted in yellow is attached as a supplement to this comment. The outline of the original manuscript was:

1. Introduction

2. Methods

2.1 Aircraft instrumentation

2.2 Corrections to UHSAS size distributions for refractive index

2.3 Method to calculate ambient extinction

2.4 Uncertainty in calculated and measured extinction

3. Results and analysis

3.1 Parameterizing f(RH)

3.2. Relationship between κchem and κext

3.3 Constraints on the hygroscopicitiy of OA

3.4 Comparison of airborne and ground-based data

4. Conclusions

The revised manuscript diverges in structure from the original beginning in Sect. 3:

3. Results and analysis

3.1 Selection of data

3.2 Observed aerosol composition and hygroscopicity

3.3 Constraints on the hygroscopicitiy of OA

3.4 Parameterizing f(RH)

3.5 Comparison of airborne and ground-based data

4. Discussion and conclusions

Appendix

A.1 Derivation of the κext parameterization

A.2 Relationship between κchem and κext

A.3. Additional data supporting use of the κext parameterization

Supplemental Materials

To reduce the emphasis on the parameterization of f(RH), the derivation is moved to the Appendix. To provide more information on the data selection, the hygroscopicity of the aerosol, and its vertical structure, new sections 3.1 and 3.2 and two new figures have been added. These are followed immediately by a discussion of constraints on the hygroscopicity of the organic aerosol provided by our observations. Only then is the new parameterization introduced and used. In the Supplemental Materials and Appendix we provide further evidence from the literature and from additional measurements to support the use of this parameterization.

In addition to these changes we have strengthened the discussion of uncertainties in our measurements and provided more detail on the calibration of the extinction measurements.

The following new figures have been added:

Figure 2: Map of flight tracks and locations of profiles Figure 3: Vertical profile from 2013/06/22 showing vertical structure Figure 4: Composite vertical profile from all se-

lected individual profiles showing median, interquartile, and interdecile values Figure 5: f(RH) at ~70% and ~90% RH calculated from the composition and size distribution measurements, and directly measured by the CRDS Figure A4: f(RH) from additional measurements in Boulder, Colorado showing hygroscopicity from 11-97% ambient RH

The original Fig. 2 has been eliminated. The original Figs. 3 and 4 have been combined in Fig. 7. The original Figs. 5, 6, and 7 have been moved to the Appendix.

Comment: Page 25700, line 21 and page 25701, line 6: What is the exact range of measured RH inside the cells? Please give the range and standard deviation. How stable is the RH during a profile? The current values given are very vague. The dry value changes within the manuscript from <15% to <25 %. At 25% RH the influence of hygroscopic growth of organic substance can become relevant.

Response: Section 2.1 now describes the range of values of RH in each channel: "Typically, one elevated-RH channel measured at ~70% RH (actual range 70-73%) and the other measured at ~90% RH (actual range 86-94%). Data were excluded from analysis when the RH of the high RH channel was <85%." The dry channel "measured at ~15% (actual range 8-23%)." Fig. 3 gives an example of the stability of the RH control during profiles. Histograms of the actual RH values are reported in the Supplemental Materials.

Comment: Page 25700: As mentioned above, it should be clearly stated which profiles were selected and which criteria were applied. Showing the average profiles of f(RH) and case studies would improve the quality of the paper.

Response: The selection criteria are described more in the new Sect. 3.1, and we have added a citation to Wagner et al. (2015), who describe in great detail the selection of the profiles and the compositing technique. Figure 2 now shows a map of where the observations were made.

Comment: Page 25701, line 10: Were the calibration measurements with ammonium

sulfate conducted before each campaign or flight? Please show (at least in the reply letter) the corresponding calibration plot and state the degree of agreement in the revised manuscript. Presenting this information is critical to evaluating the usefulness of the proposed parametrization.

Response: The CRDS has been described in detail in Langridge et al. (2011), who tested the hygroscopic response of the instrument to inorganic salts and polystyrene particles. The fact that the CRDS system is not routinely calibrated is discussed; it is a fundamental technique that is occasionally checked with an absorbing gas (ozone). More important to the measurement of f(RH) is the transmission efficiency of the particles, which we now describe in more detail, and the accuracy of the RH sensors and their calibration, which we also discuss now. These issues appear in the last two paragraphs of Section 2.1.

Comment: Sect. 2.1: How were particle losses (from the inlet to the CRDS and within the CRDS) characterized and how were they treated in the data analysis?

Response: Section 2.1 now describes the losses in the inlet and plumbing system, which are very small for the <0.7 μm particles we analyze.

Comment: Page 25702, line 7: The low amount of particle light extinction above 700nm is surprising to me. What was the exact range for all analysed profiles? Could this be due to losses inside the aircraft sampling lines? In the reviewers opinion, it is important to keep the influence of the coarse mode in mind since it has (even at low number concentrations) an important impact on the overall f(RH) (see e.g. Zieger et al, 2013, 2014).

Response: Since our analysis is limited to measurements of particles <0.7 μm, we don't address the coarse mode aerosol. However, Brock et al. (2016; Part II) show that the coarse mode is a small fraction of the total extinction, and retrieve aerosol optical depths that are consistent with regional climatology. The coarse mode is not a major contributor to aerosol extinction in the southeastern U.S. in summertime in typical conditions.

Comment: Sect. 2.2: How were the Mie ambiguities (or Mie wiggles) treated in the UHSAS size correction?

Response: Because the UHSAS uses a 1053 nm laser, the Mie oscillations occur at larger sizes than considered here. The wavelength and wide scattering angles ensure a monotonic response for reasonable refractive indices (see Cai et al., 2008), although there is reduction in resolution for sizes larger than about 0.7 μm due to curve flattening.

Comment: Sect. 2.3: The usage of k-Köhler theory to calculate optical enhancement factors and related closure studies has also been done in previous studies, which should be referenced here (see e.g. Zieger et al., 2013).

Response: We discuss more thoroughly the literature in the introduction, and in the final section we compare our results to others, including Zieger et al. (2013). Further, we use data digitized from graphs in Zieger et al. in the Supplemental Materials to further support the use of the κext parameterization.

Response: Sect. 2.4 (second last paragraph on page 25709): Please state also the relative uncertainties in f(RH) for the three RH channels.

Response: The last sentence of Sect. 2.1 now reads, "Thus the uncertainty in f(RH) is estimated to be ±11% and ±16% for the medium and high RH channels, respectively. This uncertainty estimate does not account for possible residual water present in particles in the ∼15% RH channel, which could bias the f(RH) values low."

Comment: Result section, Fig. 2: Is this a ground measurement or why is it not shown as a profile? If it is a ground based measurement, why has it been chosen? Again, it would be highly desirable if the actual profiles would be shown and discussed.

Response: Figure 2 has been replaced with an example profile (Fig. 3).

Response: Fig. 2b: How does the actual f(RH) (calculated vs. measured) compare at

the three RH's?

Response: Figure 2 has been replaced with an example profile (Fig. 3). Figure 5 now compares calculated and measured f(RH) using a fixed κorg of 0.05 at the medium and high RH values for all the data.

Comment: Sect. 3.1: Defining the parametrization at RH=0% as 1 cannot be realistic for actual atmospheric conditions (due to hysteresis effects). I understand that this assumption is needed due to the limited amount of RH channels, however, a systematic error in one of the elevated RH cells could also explain why the fit is not a suitable parametrization. This is one reason why the authors have to include their instrument calibration with known hygroscopic salts and a discussion on particle losses in the revised manuscript. In addition, I find it astonishing that only a short time period (8 July 2013, 11:10-11:45) is chosen for their fit (Fig. 4a) and time series (Fig. 2a), from which it is even not clear if it is an actual airborne profile or not.

Response: In the Supplemental Materials we show that the new parameterization does a better job than the power-law gamma parameterization for several higher resolution f(RH) cases from the literature. In Section A.3 we show the previously unpublished data that of f(RH) with continuous deliquescence behavior for a different environment. Remember also that we are measuring the deliquesced aerosol, and that it is heavily organic in composition. Of course we have never claimed that this parameterization is always better than other choices, and provide several examples of where it should not be used in Appendix A.1. We also discuss in Sect. 3.4 (last two paragraphs) the limitations on the use of this parameterization. The κext parameterization was applied to all of the data, not just to a short time period. We found that it fit better than the gamma parameterization for more than 2/3 of our profiles, and that there are strong physical arguments for the parameterization we have developed, when applied to an organic-dominated submicron aerosol.

Comment: Page 25711, line 26: I doubt that the change in refractive index from dry to elevate RH only has an approximate effect of 20% and thus can be ignored to first order. For example, if one takes the hygroscopic growth factor of a 200nm ammonium sulfate particle (at RH=90 %) to be approx. 1.7 then this will give at RH=90% a refractive index of ∼1.36 (if calculated using a volume mixing ratio). The change in scattering alone will be more than 20% (at RH=90 %) and depending on the mode diameter up to 1 _m it will be rather a factor of _1.5 to 2.5. Please clarify and proof you assumptions e.g. by showing a further sensitivity study that accounts for changes in refractive index (e.g. by adding the extinction efficiency for m = 1:36 and m = 1:33, for pure water to Fig. 5).

Response: Please note that we are arguing that the functional form of the κext equation is appropriate but only approximate, not that it is a perfect predictor of the f(RH) curve from first principles. Also, because we are averaging across a size distribution, the effect of refractive index is reduced compared to your example, although it is not negligible. We have calculated this refractive index by comparing calculated extinction with no refractive index change to calculated extinction with a reduced refractive index from water for all of the analyzed data. As we now state in Sect. A.1, "The volume-extinction approximate proportionality in Eq. (A1) applies for an aerosol of constant refractive index, which is not the case for an atmospheric aerosol particle growing by addition of water with increasing RH (Hänel, 1976; Hegg et al., 1993). The methodology to calculate ambient extinction (Section 2.3), which incorporates the aerosol composition and size distribution measurements, can be used to estimate the effect of aerosol water on the refractive index and its impact on extinction. Using this approach, the calculated mean decrease in refractive index caused by condensed water reduces extinction by a factor of 0.81 +/- .03 for the ∼70% RH channel and by 0.71 +/- .03 for the ∼90% RH channel. Because of this effect and the rough proportionality between particle volume and extinction, Eq. A1 is only an approximation that should be used parametrically to interpolate and extrapolate from discrete measurements on the f(RH) curve. However, it is a physically based representation of the expected functional form of f(RH), unlike alternative parameterizations."

Comment: Page 25712, line 16: I suggest to delete this sentence since an argument is brought forward in terms of a measurement result that has not been published or reviewed yet and this is hard to evaluate or judge on (and I guess it is not winter 2015 since this lies in the future).

Response: These data are now presented in the the Appendix (A.3). The previously unreported data were collected in a very different environment (winter in Colorado, with an organic and nitrate-rich aerosol) with a completely different instrument (Gordon et al., AMT, 2015). As a result we don't want to include them in the main text of this paper. But these data provide a very compelling, if limited, indication that the κext parameterization is more broadly applicable and is appropriate even at RH >95%.

Comment: Page 25715, line 16: It is not clear to the reviewer why the uncertainty of the organic _ should cancel out when calculating f(RH). A slight overestimation of the organic κ will also lead to an overestimation of the f(RH) (see e.g. Fig. 9a in Zieger et al, 2015) and vice versa. In general, due to the importance of the organic contribution the uncertainty of the organic κ will easily compensate other systematic errors. Please clarify.

Response: The uncertainties that cancel are the UHSAS uncertainties and the AMS flow uncertainty, not the uncertainty in the organic fraction. The text has been clarified: "Some of the errors in the calculated extinction–UHSAS sizing bias, UHSAS counting statistics, and UHSAS and AMS flow uncertainties (Sect. 2.4)–are not independent and should cancel when calculating f(RH)."

Comment: Page 25716 (first paragraph) and Fig. 8: Could these low organic k-values also result in the effect of a temperature dependent evaporation of inorganic component (like ammonium nitrate, see e.g. Aan de Brugh et al., 2012), which were held constant to derive the organic k?

Response: Inorganic nitrates were insignificant in the warm summertime of the southeastern U.S. We support this assertion by referencing in Sect. 2.1 the results of

Attwood et al. (2014) and Xu et al. (2015) from observations taken at the Centreville, Alabama ground site in collaboration with the airborne measurements. They report inorganic nitrate values < 0.02 μg m-3.

Comment: Table 2 is not discussed in the main text. The comparison in terms of linear regression will always be better for the extinction coefficient which is determined mainly by particle number concentration. To better evaluate the model performance to hygroscopicity measurements the authors should add a table or plot showing the comparison of the actual f(RH) modelled vs. measured. In addition, the variation in RH and the contribution of the coarse mode for each profile should be stated. Again, why were only these eight days selected?

Response: Table 2 is referenced in the fourth paragraph of what is now Section 2.4. The new Fig. 5 now shows all the calculated vs. measured f(RH) values. The data selection is detailed in Wagner et al. (2015) and is also described better in the new Section 2.1.

Comment: Fig. 3: What temporal averaging was applied here? In general, how was the data averaged?

Response: Averaging of the data to 10 s is described in the new Section 2.4.

Comment: Fig. 4b: For completeness, the ratio of calculated to measured f(RH) at RH=90% should be shown as well.

Response: The new Fig. 5 shows this ratio.

Comment: Fig. 7: Are the outliers determined by certain events or aerosol characteristics? Have the authors tested the different possibilities, e.g. by color-coding the points according to time, flight altitude, temperature, apparent coarse mode, mean geometric diameter? This could be a useful addition to evaluate the model performance.

Response: This figure is now in the Appendix as Figure A.3. We have not been able to identify any systematic attribute of the outliers. Groups of outliers are associated with

particular flights, but there doesn't appear to be any change in instrument performance, aerosol composition, or size distribution that would explain the groupings.

Comment: Sect. 3.4 and Fig. 8: Please specify how the organic mass fraction was calculated (e.g. was BC included or not).

Response: As noted in the last sentence of the old Sect. 2.2, BC was included in all calculations other than the UHSAS refractive index response correction.

Technical comments:

Comment: Page 25703, line 3: I would remove 'of a design now commercially available' since it is not relevant for this work.

Response: Since we do not have a publication for this DMA, by referencing the commercial instrument that is based on our prototype readers can obtained detailed specifications. We prefer to keep this comment.

Comment: Page 25700, line 5; page 25712, line 22: Full stop missing at the end of the sentence.

Response: Corrected.

Comment: Page 25715, line 20: Remove the 'r' behind _chem.

Response: Corrected.

Comment: Page 25697, line 2: I would suggest to remove 'meteorological, trace gas, and' since this data is not being used in the following article.

Response: These data are important in determining the vertical structure, as is now described in Sect. 3.1.

Comment: Table 1: Please mention the corresponding wavelength in the caption and unit for the density.

Response: The density units have been added. Most of the references do not provide wavelength information for the refractive index, but are invariably reported in the mid-visible, where they vary little.

Comment: Fig. 6: The x-axis is a little bit confusing and at first the reader looks at 2, 3, etc. um diameter. Better replace it by 0.2, 0.3, etc.

Response: Graph has been modified as requested.

Finally, we have reprocessed all of the extinction values calculated from the AMS and size distribution measurements using the best estimate of κchem for OA of 0.05 from our measurements, rather than the 0.076 from the literature we used previously. This improves theoretical and measured comparison of f(RH) at the high humidity condition (Fig. 5) compared to the prior value.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/15/C12352/2016/acpd-15-C12352-2016-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 25695, 2015.