Final Author Comments on "Aerosol optical hygroscopicity measurements during the 2010 CARES Campaign" by D. B. Atkinson et al.

We thank all of the reviewers for their thoughtful comments, which have helped to improve the paper. Reviewer comments are shown in black text and our response in blue.

Comment from A. Jefferson anne.jefferson@noaa.gov

Nice paper, but seems to lack some essential information. The uncertainty calculations are only for kappa values. What about the estimated uncertainty of the nephelometer growth factor, particularly a log fit involving 4 different parameters using only 3 data points? What was the spread or range of values and standard deviation? Do you get different gamma values if you use only the medium and high RH values in the nephelometer?

The uncertainty in the derived kappa (and growth factor, GF) values is related to the uncertainty in the measured f(RH) and gamma values. Dr. Jefferson raises the question of what the intrinsic uncertainty is in the gamma. Gamma can be determined from a calculation using only two points (as indicated by Eqn. 1 in the manuscript) or from fitting a line to a graph of $\ln(b_{ext})$ versus $\ln[(100\text{-}RH_{low})/(100\text{-}RH_{high})]$. For this study, we calculated the gamma values using the two-point approach and used the highest RH and low RH measurements in the calculations as stated in Section 3.2.3. In general, the two methods agree very well. At T0, there is only one period where the two differ substantially, but this followed a brief period where problems were found with the mid-RH channel measurements due to insulation that had been accidentally removed allowing a cold spot to develop that had caused condensation. Outside of this period, the 2-pt method gave gamma values that were within 5% of the 3-pt fit value. Similarly, at T1 (where the nephelometer was located) the 2-pt and 3-pt fit methods gave very similar results. For the key measurement period (June 21-27) the two methods give nearly identical results, with the average of the ratio between the 2-pt and 3-pt fit method equal to 0.97 +/- 0.016 (1 sigma standard deviation). Thus, we see that there is a very minor difference between the two methods that would not have any substantial influence on our conclusions.

What averaging time was used for the measurements?

The averaging time was 10 minutes, as stated in Sections 3.2.1 and 3.2.2.

Were truncation corrections applied to the nephelometer measurements?

Truncation corrections were not applied. But the truncation correction for the Aurora nephelometers used here amounts to only ~4% and has an even smaller influence on the fRH and gamma measurements due to cancellation of errors. Further discussion is provided below in response to Reviewer 1.

Can you explicitly state the measured RH of the low, medium and high RH values inside the nephelometers?

A time series of the high RH values is shown in Fig. S4. For T1 (nephelometer) the high RH average was 72% +/- 9%, with the standard deviation having to do with diurnal fluctuations associated with challenges in temperature control of the trailer. The average value of the low RH

for the nephelometers over the key measurement period (June 21-27) was 29% +/- 4%. This information has been added to the revised manuscript.

Were the RH sensors calibrated against a higher quality sensor?

The nephelometer's internal RH and Temperature sensors (a standard design manufactured by Vaisala, Inc.) were used during CARES and their performance was verified pre-campaign by comparison with an external sensor (EE08 by E + E Elektronik Ges.m.b.H).

Was the lowest RH within a predicted metastable range of the aerosol, i.e. above the efflourescence point of NaCl?

The efflorescence RH of NaCl is ~43%. The low RH was below this value.

Anonymous Referee #1

General comments

The paper by Atkinson et al. titled "Aerosol Optical Hygroscopicity Measurements during the 2010 CARES Campaign" presents results from the 2010 CARES study around Sacramento, CA. The paper address a well-know topic, i.e., the optical direct effect of aerosol particles through scattering and absorption of solar radiation, and how these optical effects change with other factors such as particle composition. Specifically, the paper presents measurements of the effect of water uptake on particulate light extinction or scattering made at two different locations during CARES. The water uptake is characterized through the dimensionless optical hygroscopicity parameter gamma. The author perform calculations allowing an estimate of the particle growth factor (GF) at 85% relative humidity and the dimensionless hygroscopicity parameter kappa for oxygenated organic aerosol (OA) and for supermicron particles. The derived range of oxygenated OA values are in line with previous observations. The authors explain the relatively large kappa values obtained for supermicron particles with the contributions of sea salt-containing particles. To date, there is still significant uncertainty associated with the climate forcing by ambient aerosol particles, and current climate models have to be improved in order to be more accurate at reproducing and predicting the global mean temperature. Therefore, scientific work that pertains to the optical properties of ambient aerosols, and their connections to hygroscopic and chemical properties, is very much needed. The authors make use well of tested measurement techniques and modeling, and present results that are in line with previous publication. Albeit not particularly ground-breaking in its content and in the techniques adopted, I consider this to be a valuable paper that presents results from an important air quality field study and it is definitely appropriate for publication on ACP. Notably, the authors attempt to determine the hygroscopicity of the supermicron aerosol fraction, which represents a somewhat original aspect of the paper. The paper makes a large use of modeling and this comes with some inherent assumptions that unfortunately cannot be avoided. However, the authors do a good job at addressing the uncertainties and use cross sensitivity analysis is useful to determine the relative contribution of sub- and supermicron particles to the total extinction or scattering. The manuscript is well written and clear in all the various sections. The introduction puts the work

into context of previous literature and the references are adequate and up to date. The experimental part is accurately described and the authors provide extensive detail on the instruments used to characterized the aerosol properties, and provide accurate information regarding the measurement techniques and modeling / calculations performed. The amount of material (text and figures) provided for the discussion is sufficient and clear. Regarding the concerns raised by Dr. Anne Jefferson in a separate statement (uncertainty for the nephelometer measurements and the derived growth factor as well as the truncation correction of the nephelometer itself), I agree that the authors should provide an estimate of the uncertainty of the derived gamma values in the final version of the paper. I recommend that the response that they already provided should be somehow incorporated in the paper, including the clarifications on the truncation correction to the scattering data, in order to make the paper stronger and clearer. Overall, I have a few comments and questions (see specific comments below), but I believe that the paper can be published basically as it is. I have only one question and one correction.

We thank Referee #1 for the nice comment on the clarity of our presentation. We have incorporated some of the response to Dr. Jefferson in the final draft of the paper.

Abstract, Line 9, and later in the paper: the size cut of the "supermicron" particles should be specified, as it is stated in the conclusion (defined here as particles with 1 μm< dp,a < 2.5 μm). Also, because the AMS nominally measures in the submicron range, does it mean that the authors combine submicron chemical data and supermicron optical data to determine the kappa for OA ? Do the authors use the SPLAT data for the kappa of supermicron particles ?

We will insert the definition of supermicron in the Abstract. To clarify: supermicron optical properties were not specifically measured, but the total scattering/extinction by the sub+supermicron particles. It is in our analysis that the contributions from the two modes are assessed and separated. Ultimately, the determination of the kappa for (submicron) OA was not very sensitive to the variations in the supermicron fraction of scattering/extinction, likely because the other components were highly hygroscopic. As noted in the manuscript, the composition of the supermicron fraction was treated separately (and assumed constant for the modeling, except for the highlighted period where the PALMS data was used). We decided not to use the SPLAT II data to quantitatively constrain the time-dependent variations in supermicron composition because the complementary data was not generally available at T1for the time period of interest. We do note that organics are minority species in the particles larger than 1 micron vacuum aerodynamic diameter according to the SPLAT II and limited PALMS measurements.

Introduction, Page 31207, Line 11: correct spelling of the word hygrocopicity

We have corrected the mis-spelling of the word hygroscopicity.

Anonymous Referee #2

The paper by Atkinson et al. titled “Aerosol optical hygroscopicity measurements during the 2010 CARES Campaign” presents results on the influence of water uptake on the aerosol optical

properties. The aim of study was to investigate the hygroscopic properties of oxygenated organic aerosol (OOA) and supermicron particles, based on observations made at two ground sites during the 2010 CARES field campaign. Optical closure calculations were performed between measurements of particle chemical composition, size distribution and optical properties at different relative humidity. The results showed that OOA is moderately hygroscopic and the retrieved hygroscopicity parameter κOOA is consistent with previous studies. Supermicron particles were found to be highly hygroscopic, which is consistent with substantial contributions of sea salt-containing particles in this size range. Analysis of the dependence of κsuper on chemical composition indicated correspondence between the chloride fraction on sea salt particles and κsuper. The authors attribute the variability of κsuper to atmospheric processing involving chloride displacement by nitrate and the accumulation of secondary organics on supermicron particles. The paper is somewhat original in addressing hygroscopicity of ambient particles from optical measurements. In particular, there are still lots of open questions in the hygroscopicity of ambient supermicron particles and the manuscript presents important results in this field. The experimental part is accurately described and provide extensive detail on the limitation of each instruments. The authors discuss also the limitation of the data treatment and provide information on the effect of the particles mixing state on the results. The manuscript is in the scope of ACP and is certainly suitable for publication in this journal. However, I have a few comments and questions that should be considered before publication.

General comments:

Optical closure was performed by using measured particle size distribution from SMPS and APS. Size distributions were measured up to 20 µm using the APS. The authors imputed directly the measured size distributions in Mie computation and therefore did not take into account particles larger than 2 µm (Figure S1 clearly shows missing particles larger than 2 µm). In contrast, scattering coefficients which are used for optical closure represent the overall size distribution. I recommend that size distributions obtained with the SMPS and APS to be fitted with log-normal size distributions in order to take into account the missing coarse mode particles.

The reviewer is correct that the optical closure was determined by comparing calculations that used the SMPS and APS size distributions as inputs, and also that the APS measured up to 20 um. However, due to differences in particle transmission (and in the case of the CRD instrument the use of a cyclone) scattering by particles > ~2.5-3 um aerodynamic diameter, or ~ 1.5 microns mobility diameter, was not measured here. Thus, the appropriate size distribution for use when performing the optical closure is the truncated distribution presented.

The reviewer is correct that the optical closure was determined by comparing calculations that used the SMPS and APS size distributions as inputs, and also that the APS measured up to 20 um. However, due to differences in particle transmission (and in the case of the CRD instrument the use of a cyclone) scattering by particles > ~2.5-3 um aerodynamic diameter, or ~ 1.5 microns mobility diameter, was not measured here. Thus, the appropriate size distribution for use when performing the optical closure is the truncated distribution presented in the manuscript, and log normal fitting is not required.

As underlined by Dr. A. Jefferson in her comments, truncation corrections of the nephelometer measurements should be performed. The authors answered that this correction cannot be done due to missing measurements of Angstrom coefficient. However, the correction can be performed by Mie-calculations using the retrieved size distributions, bulk real refractive index, the limited angular range and the intensity function of the nephelometer. I recommend that the authors incorporate this correction in the manuscript (Müller et al., 2009).

We have calculated Angstrom exponents from the observed campaign-average size distributions for the measured dry particles and for "wet" particles where it was assumed that fRH = 2 (a typically observed value during this study) and that all particles are equally hygroscopic. We calculate values of 0.995 and 1.032 for dry and wet particles, respectively, using the wavelength pairs 450 nm and 700 nm, which are the same wavelength pairs used in Müller et al., (2009). We had used an Ecotech Aurora nephelometer. The Müller et al. study indicates that the Ecotech neph has the smallest truncation error out of the three types tested (Ecotech, Radiance Research, TSI); the Ecotech correction factor estimated from their Fig. 3 given the calculated Angstrom exponents is 1.04, corresponding to a 4% correction that would increase the observed scattering. However, since the calculated Angstrom exponent values are very similar and since the variation of the correction factor with the Angstrom exponent is relatively slow, the correction factor will be almost identical for the dry and wet particle distributions. No equation is given to allow us to calculate explicitly the correction factors at our calculated Angstrom exponents, but we estimate the ratio (using a data extraction program) between the correction factor for dry and wet particles to be 1.0033, corresponding to an 0.3% change in the f(RH). Such negligible differences will have negligible consequences for our observations or conclusions. We have added a condensed version of this discussion to the main text in section 3.2.2.

Nephelometer measurements can suffer from heating induced by the lamp within the cell of the instrument. This heating can be critical for your measurements since it can cause a reduction of the sample RH and thus an underestimation of f(RH) (Kus et al., 2004). Did the authors use the RH at the entrance of the nephelometer or within the cell for γ calculations ? If they used the RH at the entrance of the nephelometer, a correction for the sample RH must be applied or they should indicate at least the errors on RH, γ and κ induced by the heating.

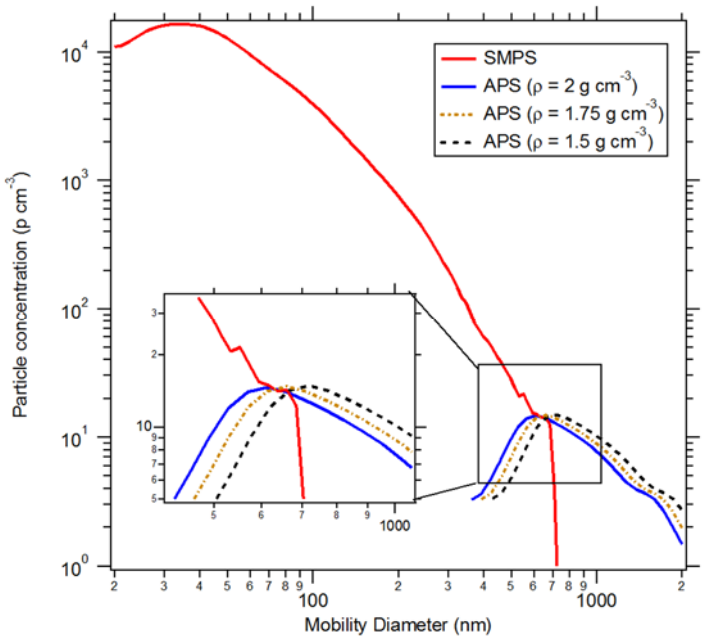
Again the Referee makes a salient observation about many nephelometer measurements that are used to investigate the dependence of scattering on RH, but the instrument that was used in the construction of the humidigraph uses a new type of source that is based on LEDs (which have much better light to total power ratios than incandescent sources that were used in the past) that is purported (by Aurora) to cause much less heating of the sample flow. More importantly, the RH and T measurements were made in the scattering zone of the nephelometer and agreed with the comparison measurements made outside of the nephelometer, these manufacturer's claims seem to have been borne out.

The authors assumed a single density value to convert aerodynamic size distributions to equivalent size distributions. Size distributions in Figure 1 C and F does not always seem to fit

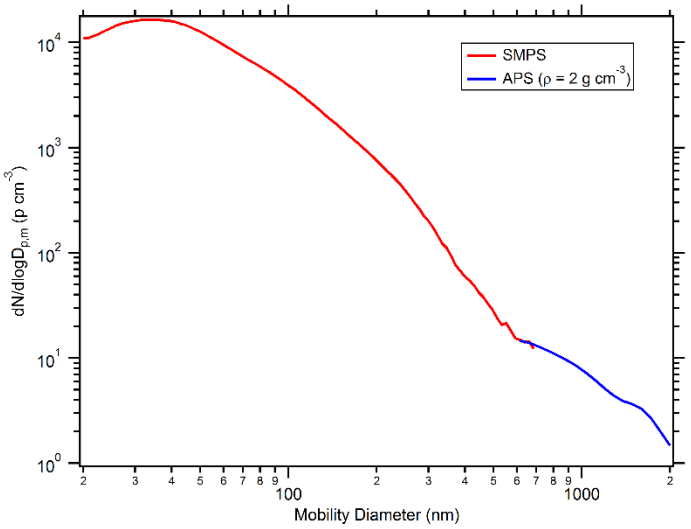
well together. Did you check the overlapping of SMPS and APS size distributions throughout the campaign? The authors could show an example of overlapping of SMPS and APS size distribution (in Figure S1 for example) and estimate the error on the calculated parameters (γ and κ) due to the assumption of a single density value throughout the campaign.

The measured average SMPS distribution and (density-adjusted) APS distributions from T0 are shown in the figure below. We have assumed a density of either 2, 1.75 or 1.5 g cm^{-3}; smaller values do not seem likely for supermicron particles. At least from this average picture, it is clear that the rho = 2 g cm^{-3} provides for much better overlap with the SMPS distribution compared to the rho = 1.5 g cm^{-3} assumption. The rho = 1.75 g cm^{-3} also provides for reasonable overlap, although the rho = 2.0 g cm^{-3} case does a bit better. (The rapid fall off in the SMPS at large sizes and in the APS at small sizes are simply instrumental artifacts due to undercounting of particles at the limits of the ranges.) The figure shows results for the campaign average; doing a similar comparison on a point-by-point basis is more challenging because of increased noise associated with the individual scans. We had done this comparison early on in our analysis and decided that the rho = 2 g cm^{-3} case gave the best overall overlap, and also was consistent with the particle composition measurements from the single particle instruments. Use of a smaller density would have led to a larger calculated extinction/scattering, ~8% and 20% larger for rho = 1.75 and 1.5 g cm^{-3}, respectively. However, this increase would have occurred for both the dry and wet particles, and consequently has minimal impacts on the calculated fRH and, thus, the derived kappa values. Using the average size distributions, we estimate the influence here by calculating a bulk average growth factor given fRH = 2, for simplicity treating all particles identically. We find that the GF increases as density decreases, but only by a small amount, changing from 1.335 to 1.345 to 1.355. These values correspond to kappa values of 0.246, 0.256 and 0.265 (assuming RH = 85% and a dry particle diameter of 1000 nm, using the Equations of Petters and Kreidenweis). Thus, the assumption of constant density might be contributing to a slight underestimate in the kappa values during certain time periods, but this underestimate will be overall quite small and within the stated uncertainties already reported. As suggested by the reviewer, we have updated Fig. S1 to show the overlap between the two instruments when the density = 2 g cm^{-3} (see below). We have also added the following text to the manuscript:

> "The merged size distributions were ultimately used as input to the Mie theory calculations (see next section), and thus the assumption regarding the particle density will have some influence on the calculated scattering. It is unlikely that the particle density is much larger than 2 g cm^{-3} Had smaller values been assumed, the shift in $d_{p,a}$ to $d_{p,m}$ would have been smaller and, consequently, the calculated scattering would be increased. Had a density of 1.75 or 1.5 g cm^{-3} been assumed, the calculated scattering would have increased on average by ~8% or 21%, respectively. This is important to keep in mind in the context of the dry particle optical closure presented below. However, a density of 2 g cm^{-3} gave the best overlap with the SMPS distribution, on average, and thus was chosen here; the average SMPS and APS mobility size distributions are shown for the T0 site in Fig. S1 for reference. Additionally, since the hygroscopicity measurements result from a ratio of extinction or scattering values, these effects largely cancel out and lead to only minor changes in the derived hygroscopicity parameters."



Example Figure.



Updated Figure S1. The average supermicron mobility size distribution from the APS at T0 used to estimate the large particle contributions during the "missing" data period is shown in blue, along with the average SMPS distribution determined over the same time period. Note that the f(RH) and γ model calculations are not particularly sensitive to the shape of the assumed supermicron size distribution because the scattering efficiency Q starts to reach an asymptotic limit in the supermicron size range. There is good overlap between the SMPS and APS size distributions.

Specific comments:

Paragraph 3.1, page 31208, line 14 : Please replace (Zaveri et al., 2012) by Zaveri et al. (2012).

Paragraph 3.2.2, page 31209, line 24-25 : Please indicate the three RH values.

Paragraph 3.4, page 31214, line 6 : Please replace (Setyan et al., 2014) by Setyan et al. (2014).

Table 1: Please add references of the values used for model calculations.

We have made these changes.

Anonymous Referee #3

The paper presents an analysis of the effect of water uptake on particulate light extinction and scattering during the CARES 2010 study. The analysis includes a comparison of measured and calculated gamma values as well as a determination of kappa values for different aerosol chemical species and for supermicron particles. Very little attention has been paid to the hygroscopic growth of supermicron particles making this is a novel aspect of this study. The paper is well written and the data are presented very clearly. The paper is publishable in ACP after the minor comments below have been addressed.

p. 31206, lines 23 – 25: Particle hygroscopicity is also characterized by comparison of low and high RH size distributions. It would be more accurate to state here that comparison of low and high RH extinction and scattering coefficients is one method commonly used to characterize particle hygroscopicity.

We have modified the sentence to read "One common method used to characterize particle hygroscopicity is through comparison between the light extinction or scattering coefficients…"

p. 31212, Line 27: Chemically, what is the difference between POA and HC?

Average mass spectra of particles that were classified into classes labeled POA and HC both have mass spectral peaks at m/z= 43, 41, 39, 27, 55, 57, 67, 69, 71, 77, 83, 95, etc. – very similar to the AMS HOA mass spectrum. However, the mass spectra of particles that belong to POA and HC classes are different enough to be classified into different classes – while HC is dominated by low m/z peaks, POA particles have larger fraction of PAHs. Moreover, the temporal evolution of these two particle types are different.

p. 31214, Line 11: The APS actually quantified particle number concentrations up to 20 um?

The APS measured particles up to this size, and attempts were made to minimize losses to the APS. However, as the optical instruments only measured particles smaller than ~3 microns this larger size range is inconsequential. A link to the manufacturers' description is provided here, for reference:
http://www.tsi.com/uploadedFiles/_Site_Root/Products/Literature/Spec_Sheets/3321.pdf

Figure 1c: Based on this figure, the SMPS and APS data do not appear to line up very well. Explanation?

The data overlap better than it visually appears from this figure. Please see the response to Reviewer 2 and the associated figure for a demonstration of the good overlap between these instruments.

Figure 3 caption: The four panels should be described in order, i.e., 3a, 3b, 3c, and 3d. Or at least 3a and 3c, then 3b and 3d.

We have modified the caption.

p. 31221, Lines 21 – 23: The statement that gamma at T0 and T1 are similar during the latter part of the study is not apparent from the figure. Observed values are higher during this period at T1 compared to T0.

Discussion of the observation in question was removed from the text. It was based on an examination of the data from the full campaign, some of which was not used in this paper for reasons that were explained in the Experimental section of the manuscript.

Figure 5: It would be helpful to have a color scale to refer to.

We have added color scales to the figure.

p. 31227, Lines13 – 15: It would be more appropriate to cite references that measured ocean-derived sea spray aerosol rather than tank/laboratory derived. I suggest Keene et al., JGR, 2007, Facchini et al., GRL, 2008 or Quinn et al., Nat. Geoscience, 2014.

Thank you, we have included those references in the revised manuscript.