

## **Response to anonymous referee comments on “Size-resolved aerosol composition and link to hygroscopicity at a forested site in Colorado” by Levin et al.**

We thank both anonymous referees for their helpful comments and suggestions for improving our manuscript. Detailed responses to each point are given below. Author responses are indented and quotations from the revised manuscript are in italics.

### **Anonymous Referee #1**

The manuscript describes ambient measurements of cloud condensation nuclei (CCN) concentration and fine particle chemical composition during a six-week campaign in a forested site in Colorado. The authors discuss particle hygroscopicity at the light of organic and inorganic species concentration in particles smaller than 350 nm. The results of this study are then used to investigate seasonal variation in particle composition observed during a one-year long field experiment at the same site. The main conclusion of this work relates to the hygroscopicity parameter  $\kappa$ . Assuming a known hygroscopicity for the inorganic fraction of fine particles, composed mainly by ammonium sulfate, the best estimate of  $\kappa$  for biogenic secondary organic aerosol (SOA) is 0.13, and does not depend on particle size. This finding supports the limited literature results regarding parameterization of biogenic SOA hygroscopicity based on ambient measurements. Overall the manuscript is clear and exhaustive. The study is properly put into the context of the existing literature and the current knowledge.

### **Major comments:**

The conclusions are based on a series of assumptions including knowledge of aerosol component density, knowledge of inorganic aerosol  $\kappa$ , negligible concentration of dust and black carbon in particles smaller than 350 nm, and internally mixed aerosol. Literature works cited in the manuscript proves that most of these assumptions hold. The internal mixing assumption is not discussed in the text, but it is reasonable, considering that the site is a background area not affected by fresh primary emissions. Nevertheless, the assumption about black carbon needs further discussion. The authors claim that BC mass fraction is below 5% in fine particles (the term “fine” usually refers to PM<sub>2.5</sub> or PM<sub>1</sub>). No information is given about BC mass fraction in the size range considered in this study (particles smaller than 350 nm). To support the assumption that BC is not affecting particle mass below 350 nm the author should add some information about expected size distribution of fresh and processed BC, for example citing literature studies (Onasch et al., 2012; Massoli et al., 2012). Since no data on BC size distribution are available, it would be useful to clarify what would be the effect of BC presence on the estimated  $\kappa$ . Evaluate also if BC presence could affect density calculation and thus the conversion of vacuum aerodynamic diameter into mobility diameter.

Size resolved refractory black carbon (rBC) was measured during BEACHON-RoMBAS with a single particle soot photometer (SP2). These data were not available when this work was originally submitted to ACPD and thus we were only able to make the

statement that BC fraction was less than 5% of fine particle mass based on personal communication. However, these data are now discussed in the BEACHON-RoMBAS overview paper recently accepted for publication in ACPD (Ortega et al., *in press*). The SP2 results show that averaged over the BEACHON-RoMBAS study period, rBC was less than 4% of the total aerosol mass at all sizes, with a peak fractional contribution between 100 – 200nm. Averaged across the size range we are interested in for this work, rBC contribution was only about 2%. Including this rBC fraction in the AMS  $\kappa$  calculations decreases the study averaged  $\kappa_{AMS}$  by 0.0035, or 1.6%. This is much smaller than the uncertainty in the AMS measurement. Likewise, including the rBC fraction, with an assumed density of  $1.8 \text{ g cm}^{-3}$ , increases the study averaged bulk aerosol density by only 0.4%. While rBC can definitely play an important role in aerosol concentration in polluted environments or regions impacted by smoke plumes, these measurements indicate that it was negligible during BEACHON-RoMBAS.

We have changed the reference to rBC concentration in the paper from a personal communication to the ACPD BEACHON-RoMBAS overview paper as follows:

*“...during BEACHON-RoMBAS black carbon measured with a single particle soot photometer (SP2; Droplet Measurement Technologies) accounted for only 2% of the aerosol mass averaged across all diameters below 350 nm (Ortega et al., in press)...”*

Further, in response to Referee #2, below, we also now discuss our assumptions about internal mixing.

### **Minor comments:**

In the discussion section the authors mention that a larger variability of  $\kappa$  has been observed for aged SOA (Page 23827, line4). It would be useful to present these data in the introduction (for example at page 23819, line 17), referring to smog chamber experiments and ambient observations in SOA dominated environments (Pringle et al., 2010; Pierce et al., 2012; Jimenez et al., 2009).

At the referee’s suggestion we have moved this to the introduction.

Page 23822, line 12. Limit of detection of daily average organic and sulfate are presented. It is not clear if these limits are measured with the “mass Spec” mode or with the pTOF mode. Since the discussion focuses on the concentration data from pTOF analysis, it would be recommendable to report detection limit for pTOF data in the investigated size range (50-350 nm).

The detection limits mentioned in the paper were for the MS mode, as is commonly reported for AMS measurements. The MS mode data were used to renormalize the PToF data, but otherwise were not used in this work. From 20 – 800 nm,  $3\sigma$  detection limits for the PToF data calculated from filter measurements increased roughly linearly from

0.17 – 0.43  $\mu\text{g m}^{-3}$  for organics and 0.015 – 0.06  $\mu\text{g m}^{-3}$  for sulfate. We have changed the detection limits mentioned in the paper to those for the PToF mode.

Further, we were previously incorrectly applying the MS detection limits to the PToF data. We have corrected this and updated Figures 1 – 4. Use of the correct detection limits screens out more of the AMS data, especially at diameters below ~50 nm, but does not change the main points or conclusions of our paper.

Page 23823, line 14. Sentence is misleading. It is correct to neglect dust contribution to particle population below 350 nm, but it is not correct for the “accumulation” mode particles. Please clarify that the authors actually refer to the particle size range here investigated.

The wording has been changed to more accurately describe the aerosol size range we are measuring.

*“Thus, for this study we assume that the aerosol below 350 nm diameter was composed mainly of...”*

## Anonymous Referee #2

In the present paper Levin et al., have presented the size-resolved CCN measurements from a mountainous site in Colorado during the six-week BEACHON-RoMBAS campaign. The dataset reported appears to be of good quality and can make good contribution, as pointed out by Referee #1, in enhancing our understanding related to hygroscopicity of ambient biogenic SOAs. I believe that manuscript adequately meets the standards of Atmospheric Chemistry and Physics (ACP). I, however, have following comments, which Authors might want to address before manuscript is considered for publication in ACP.

### Comments:

1. I echo the suggestion raised by Referee #1 that conclusions are based on series of assumptions. In my opinion under certain scenario these assumptions may tend to bias the results considering that information is not available regarding the internal mixing (and to an extent about external mixing) of the aerosols. Su et al., (2010) have demonstrated the spread of  $\kappa$  in the aerosol particle of same size to investigate the internal mixing. Hence, the lack of data about internal mixing could be crucial. In the present study no detailed discussion is presented about the assumption about internal mixing of the aerosol particles in the CCN active size range.

One of the main conclusions of this work is that there is a change in aerosol composition, and thus hygroscopicity, with size. At higher supersaturations, that is smaller activation diameters, we observed a decrease in  $\kappa$  corresponding to an increased organic mass fraction. Therefore, the aerosol measured during BEACHON was not perfectly internally mixed across our measurement size range, and we do not make that assumption. However, to calculate  $\kappa$  we fit distributions of activated fraction ( $N_{CCN}/N_{CN}$ ) with a single Gaussian cumulative distribution function, taking the midpoint of this curve, where 50% of the particles were activated, as the critical activation diameter. For a given dry diameter we are therefore calculating a single  $\kappa$  value. If the aerosol at that size is internally mixed this  $\kappa$  value will represent the  $\kappa$  for any aerosol at that size. However, if there are externally mixed aerosol populations, this value will represent an average  $\kappa$  for particles at that size. Both Su et al (2010) and Petters et al (2009) show that externally mixed aerosol with different  $\kappa$  values will result in bi-modal distributions of activated fraction or distributions that never reach a value of 1. During BEACHON we did not observe either of these phenomena, and thus conclude that at a given activation diameter the aerosol was internally mixed or at least contained aerosol with similar hygroscopicity. We have added an explanation of our assumptions about internal mixing to the end of section 3.1.

*“Further, the size resolved CCNC measurements provide a single  $\kappa$  value for each critical activation diameter. If the aerosol at that size is internally mixed, this  $\kappa$  value will be representative of any particle at that size. However, if there are externally mixed aerosol populations at the  $d_c$ , the calculated  $\kappa$  value will represent an average  $\kappa$  for particles at that size. Both Su et al (2010) and Petters et al (2009) show that externally mixed aerosol with differing  $\kappa$  values will result in a bi-modal distribution of activated fraction or distributions that never reach a value of 1. During BEACHON-RoMBAS we*

*did not observe either of these phenomena, and thus conclude that at a given activation diameter the aerosol was internally mixed or at least contained aerosol with similar hygroscopicity.”*

2. I wish authors could have given little more details about the measurement setup (mostly flows through various instruments used) and estimated uncertainties in the CCNC calibration. As described by Rose et al., (2008) choice of Köhler model and calibration accuracy can strongly affect the estimated supersaturation; more so for the lower supersaturation. These uncertainties could be further crucial in estimating/calculating the  $\kappa$  by means of huge under- or over-estimations. At least authors could consider adding a line addressing this.

Levin et al. (2012), referred to in this work, give a more thorough description of the instrument setup and flows. However, at the request of the referee we have added the instrument flow rates to this paper as well.

*“Briefly, we used a differential mobility analyzer (DMA; TSI 3081), operating at a 10:1.5 sheath to sample flow ratio, to select particles in 20 different size bins between ~14 and 350 nm in diameter. The quasi-monodisperse sample was then split and sent to a condensation particle counter (CPC; TSI 3010), 1 LPM, and a cloud condensation nucleus counter (CCNC; Droplet Measurement Technologies), 0.5 LPM.”*

In reference to calibration uncertainty, we use the online aerosol inorganics model (Clegg et al., 1998), as stated in the paper. While Rose et al.(2008) found large discrepancies in supersaturation based on which Köhler model they used, these discrepancies are largely due to water activity parameterization. Rose et al, recommend using the AIM model which is highly accurate in calculating water activity for dilute ammonium sulfate solutions with uncertainties as low as  $10^{-6}$ - $10^{-5}$ .

For the BEACHON study we calibrated at each supersaturation almost every day (repeat time between calibrations at the same temperature setting was ~25 hr) and across the entire study period the standard deviation in supersaturation was  $\pm 5\%$ , very similar to the results of Rose et al. However, this does not represent the uncertainty in the calibration but rather the variance, likely due to changes in trailer temperature. When calculating  $\kappa$  from measured activation diameter we used the most recent calibration data at the same CCNC temperature setting, not the study averaged value. The uncertainties we report for the CCNC derived  $\kappa$  is calculated from the uncertainty in the curve fitting, weighted by the CCN and aerosol concentrations.

3. The density assumption/calculations are not quite clear to me. May be authors could consider elaborating the details at appropriate places in the revised manuscript.

We used assumed densities for the organic and inorganic fractions to compare mass concentration measured by the AMS and volume fractions calculated from  $\kappa$  using Eq 2. In the original manuscript this was stated on page 2386 where we calculate aerosol mass

from  $\kappa_{CCNC}$ , but was not mentioned on page 23827 where we calculate  $\kappa_{AMS}$  from AMS mass measurements, perhaps leading to some confusion. The wording on page 23827 has been changed to clarify the calculations performed here.

*“We also calculated daily averaged  $\kappa$  distributions from the AMS organic and inorganic mass measurements ( $\kappa_{AMS}$ ). To do this, we first converted AMS measured mass to volume fractions using the assumed densities mentioned above and then used Eq. 1. and the best fit value of size-independent  $\kappa_{org}$ , 0.13, to calculate  $\kappa_{AMS}$ ”*

4. Please note that on page 23826 line 17 what authors refer to cloud processing may not be true in this case as Fors et al., (2011) and Hao et al., (2013) reported their results under different scenario. Authors might reconsider this sentence.

The referee is correct that we did not measure in cloud as was done by Hao et al. (2013), however, Fors et al. (2011) present long term measurements of continental background aerosol as we do in this work. Hao et al. measured enhanced sulfate concentrations in cloud processed aerosol while Fors et al. suggested that the enhanced hygroscopicity at larger sizes in their measurements could be the result of cloud processing. To clarify this in the manuscript we have changed this section as follows:

*“Given this enhanced inorganic fraction and the lack of local sulfate emissions, it is most likely that the inorganic aerosol was more aged and may have undergone some cloud processing, as cloud droplet residual particles have been shown to have increased sulfate concentrations (Hao et al., 2013). Similarly, enhanced hygroscopicity for particles larger than  $\sim 100$  nm was observed by Fors et al. (2011) during long term measurements at a background site in Sweden. This increased hygroscopicity was also attributed to an enhanced inorganic component due to cloud processing.”*

5. Referring the Fig. 1 on certain occasions the agreement between CCN  $\kappa$  and AMS  $\kappa$  shows considerable disagreement. Do authors have any explanation? Not sure if AMS mass was too low during this period.

As the referee suggests, the discrepancies between  $\kappa_{AMS}$  and  $\kappa_{CCN}$  at all but the lowest  $s$  setting appear to be due to low AMS mass concentration at the critical diameter. With the use of corrected detection limits, discussed in response to referee #1, most of these time periods have now been screened out. Differences between  $\kappa_{CCN}$  and  $\kappa_{AMS}$  at the lowest  $s$  setting are already discussed in the paper.

6. Fig. 3 y-axis can be scaled from 0.4 to 1

We have changed this figure as suggested.

7. Please note that Jurányi et al have also reported similar low kappa values from Boreal forest measurements. Authors might consider having couple of sentences comparing their results.

Jurányi et al (2011) present 17 months of CCN and  $\kappa$  data from the high alpine research station on Jungfraujoch. Averaged over the whole study they calculated a  $\kappa$  value of 0.2, lower than the commonly assumed  $\kappa_{continental}$  value of 0.3, similar to what we found in our study. We have added a reference to their work in the introduction where we discuss  $\kappa$  values in remote areas.

8. Why very few measurement results are presented from TDCIMS measurements?

The TDCIMS data of the aerosol organic mass fraction, presented in Figure 3, represents the average organic mass fraction of 30 nm diameter particles from two measurement periods: 3 – 8 August and 15 – 18 August 2013. During BEACHON-RoMBAS, we rarely observed particles smaller than 30 nm in mobility diameter. Because of this, we typically operated the TDCIMS in two sampling modes: mobility classifying particles at 30 nm in diameter, and bypassing the mobility classifier in order to collect all particles that were sampled and charged by our unipolar charger (that is, not size-selected). Because the mobility-classified particles are most appropriate for the presentation of size-resolved aerosol composition, we just included particle composition at 30 nm mobility diameter.

We have added a few sentences to the manuscript to better explain the TDCIMS data and sampling period.

*“Due to the low mass concentrations at smaller sizes, during BEACHON-RoMBAS size selected TDCIMS measurements were only made at 30 nm. The data presented here are from two measurement periods: 3 – 8 August and 15 – 18 August 2013.”*

## References:

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system H<sup>+</sup>-NH<sub>4</sub><sup>+</sup>-SO<sub>4</sub><sup>2-</sup>-NO<sub>3</sub><sup>-</sup>-H<sub>2</sub>O at tropospheric temperatures, *Journal of Physical Chemistry A*, 102, 2137-2154, 1998.

Fors, E. O., Swietlicki, E., Svenningsson, B., Kristensson, A., Frank, G. P., and Sporre, M.: Hygroscopic properties of the ambient aerosol in southern Sweden - a two year study, *Atmospheric Chemistry and Physics*, 11, 8343-8361, 10.5194/acp-11-8343-2011, 2011.

Hao, L. Q., Romakkaniemi, S., Kortelainen, A., Jaatinen, A., Portin, H., Miettinen, P., Komppula, M., Leskinen, A., Virtanen, A., Smith, J. N., Sueper, D., Worsnop, D. R., Lehtinen, K. E. J., and Laaksonen, A.: Aerosol Chemical Composition in Cloud Events by High Resolution

Time-of-Flight Aerosol Mass Spectrometry, *Environmental Science & Technology*, 47, 2645-2653, 10.1021/es302889w, 2013.

Juranyi, Z., Gysel, M., Weingartner, E., Bukowiecki, N., Kammermann, L., and Baltensperger, U.: A 17 month climatology of the cloud condensation nuclei number concentration at the high alpine site Jungfraujoch, *Journal of Geophysical Research-Atmospheres*, 116, 10.1029/2010jd015199, 2011.

Levin, E. J. T., Kreidenweis, S. M., McMeeking, G. R., Carrico, C. M., Collett, J. L., and Malm, W. C.: Aerosol physical, chemical and optical properties during the Rocky Mountain Airborne Nitrogen and Sulfur study, *Atmospheric Environment*, 43, 1932-1939, 10.1016/j.atmosenv.2008.12.042, 2009.

Levin, E. J. T., Prenni, A. J., Petters, M. D., Kreidenweis, S. M., Sullivan, R. C., Atwood, S. A., Ortega, J., DeMott, P. J., and Smith, J. N.: An annual cycle of size-resolved aerosol hygroscopicity at a forested site in Colorado, *Journal of Geophysical Research-Atmospheres*, 117, D0620110.1029/2011jd016854, 2012.

Ortega, J., Turnipseed, A., Guenther, A. B., Karl, T. G., Day, D. A., Gochis, D., Huffman, J. A., Prenni, A. J., Levin, E. J. T., Kreidenweis, S. M., DeMott, P. J., Tobo, Y., Patton, E. G., Hodzic, A., Cui, Y., Harley, P. C., Hornbrook, R. S., Apel, E. C., Monson, R. K., Eller, A. S. D., Greenberg, J. P., Barth, M., Campuzano-Jost, P., Palm, B. B., Jimenez, J. L., Aiken, A. C., Dubey, M. K., Geron, C., Offenberg, J., Ryan, M. G., Fornwalt, P. J., Pryor, S. C., Keutsch, F. N., DiGangi, J. P., Chan, A. W. H., Goldstein, A. H., Wolfe, G. M., Kim, S., Kaser, L., Schnitzhofer, R., Hansel, A., Cantrell, C. A., Mauldin, R. L., and Smith, J. N.: Overview of the Manitou Experimental Forest Observatory: Site 1 description and selected science results from 2008-2013, *Atmospheric Chemistry and Physics Discussions*, *in press*.

Petters, M. D., Carrico, C. M., Kreidenweis, S. M., Prenni, A. J., DeMott, P. J., Collett, J. L., and Moosmuller, H.: Cloud condensation nucleation activity of biomass burning aerosol, *Journal of Geophysical Research-Atmospheres*, 114, 16, D2220510.1029/2009jd012353, 2009.

Rose, D., Gunthe, S. S., Mikhailov, E., Frank, G. P., Dusek, U., Andreae, M. O., and Poschl, U.: Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment, *Atmospheric Chemistry and Physics*, 8, 1153-1179, 2008.

Su, H., Rose, D., Cheng, Y. F., Gunthe, S. S., Massling, A., Stock, M., Wiedensohler, A., Andreae, M. O., and Poschl, U.: Hygroscopicity distribution concept for measurement data analysis and modeling of aerosol particle mixing state with regard to hygroscopic growth and CCN activation, *Atmospheric Chemistry and Physics*, 10, 7489-7503, 10.5194/acp-10-7489-2010, 2010.



