

Interactive comment on “Hygroscopic growth and droplet activation of soot particles: uncoated, succinic or sulfuric acid coated” by S. Henning et al.

Anonymous Referee #2

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In this manuscript the water uptake of different types of uncoated and coated soot particles is investigated. Different methods based on mobility analysis and/or optical sizing are used for the determination of the particles' hygroscopic growth at sub-saturation. CCN counters are used for measurement of the activation at supersaturation.

I believe that this manuscript has some potential. The manuscript clearly reports important results; however the presentation has some weaknesses. Overall I find the paper includes insufficient analysis and discussion. In addition, I believe that part of the findings are misinterpreted. I cannot support this manuscript being published in ACP as it is. The manuscript needs major revisions.

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General comments:

I have some serious doubts on the usefulness of using LACIS for measurement of soot particles. How accurate are these measurements for particles that are nonspherical and where the effective refractive index is not known a priori? In my opinion this is a very important and critical point for the interpretation of the LACIS measurements in this paper. With the HTDMA you show that the soot particles can shrink which is a clear indication that they are not spherical. For a given refractive index and fixed volume equivalent diameter the measured optical diameters are dependent on the particles morphology, fractal dimension, and the primary particle size. I assume that the growth curves from the LACIS are calculated for spherical particles with a certain (clearly specified?) refractive index. Please discuss carefully these assumptions, limitations and uncertainties and add realistic vertical error bars to the graphs. Would this explain the encountered differences in Fig 7? In line 256 it is stated that (except for the sulfuric acid coated soot) all data lies within the error bars. However, only the uncertainty in the RH measurement is considered but not the (much larger) uncertainty in the measured diameters. The disagreement observed with the sulfuric acid coated soot could arise in this case from the fact that the morphology is different. Another important criticism is that I do not agree with the explanation presented in Figure 6 (hygroscopicity suppressed by the coating). I believe it is wrong. If it were true, it would mean that the coating is not water-soluble and that more residence time in the instruments would be needed to reach equilibrium. Instead, I believe that the observations can be explained by the nonspherical nature of the particles. See Tritscher et al. (2011).

Specific comments: An overview of the most recent literature is missing in the introduction. Many statements and numbers are referenced to Horvath (1993). There is a lot of newer literature on the interaction of soot particles with water and I strongly recommend rewriting the introduction and referring to the recent literature.

Line 40: are these percentages in terms of mass or number?

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Line 52: “by nature soot particles are hydrophobic and insoluble”. That’s not generally true. For example, fuel sulfur content matters. Ship emissions (a very important BC source worldwide and not mentioned in the introduction) emit soot particles which are hygroscopic. Care should be taken with the term hydrophobic: “Pure” uncoated soot particle can be non-hygroscopic but it’s unlikely that they are hydrophobic.

Line 59: specify RH. Giving a GF without RH makes limited sense.

Line 73 and 11: Whether a particle “acts as CCN” depends on the SS. Same for “CCN activation”. If SS is high enough all particles will act as CCN. Always indicate the SS when you discuss whether a particle will act as CCN or not.

Line 90 et seq.: I did not understand the role of the NAUA and AIDA chamber. How much was the aerosol diluted? How long were the particles aged before measurement? Did you observe an influence of aging on measured properties, e.g. evaporation of coating due to the dilution? Coagulation of agglomerates is expected to change the fractal dimension and these morphology changes are expected in turn to influence hygroscopic properties.

Line 127: “. . .succinic acid was as an example for oxygenated organics substance. . .”. This compound is not a good choice for a representative model substance because it takes up no water at RH<99%. This deliquescence RH is high compared to most particle bound organics found in our atmosphere. Mention the hygroscopic properties (growth factors, deliquescence point) of succinic acid in the introduction.

Line 136 et seq. and 185 et seq. Mention that the LACIS and CCNC were operated downstream of a DMA. Did you employ a drier in front of the instruments?

Line 146: How can you be sure that two seconds are sufficient to reach equilibrium? Depending on the aerosol this might not be sufficient. What are the corresponding residence times in the two TDMA and the CCNC?

Line 150: indicate wavelength as refractive indices are wavelength dependent.

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Line 151: for dry soot a refractive index of $1.74+0.65i$ was used. The diameter of “wet particles” is retrieved with $n=1.33$. How do you know if a particle is wet or dry? Which criterion did you apply? Which refractive index is used for a particle which experiences restructuring?

Line 156: LACIS calibration with ammonium sulfate: What exactly is calibrated? The size selection of the DMA, the optical sensor or the RH measurement? Which theory describing the water uptake of ammonium sulfate did you use?

Line 162 et seq.: Which inversion was applied to the TDMA data to retrieve GF?

Line 178: It's described that the VHTDMA is able to measure the particles volatility. Could this be used to derive information on the (size dependent) coating thickness?

Line 184: How can you calibrate a humidity sensor with ammonium sulfate particles?

Line 196: Mention the total particle counter which is needed to calculate the AF.

Line 201: Its good that you calibrate you instrument frequently. But it's also important to report the encountered variability from calibration to calibration because it contains information on the instrumental stability (drifts). This comment applies also to the other instrument calibrations.

Line 204: The AMS was used to “characterize the coatings”. Please give more information, be more specific. Does it allow for a chemical and physical characterization? Together with some BC mass concentration measurements one could derive the OC fraction.

Line 214: I expect that the observed shrinking in Fig. 2 is dependent on the coating thickness and on the aging time in the chamber. In addition, it's known that this shrinking is strongly dependent on particle size. Please provide more information.

Line 216: “Activation was not observed for the different cast soot types...”. So what? This information is not very useful because activation strongly depends on particle size.

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Report the dry size and discuss this activation with respect to the corresponding Kelvin diameter. I propose to report and compare e.g. apparent kappa values (a parameterization of the particles hygroscopicity) derived from CCNC and HTDMA as done in Tritscher et al. (2011). Looking at Table 2 this should be done for all experiments. If no growth is observed with the HTDMA, the apparent kappa at subsaturation is = 0. A complication arises for nonspherical particles: the mobility diameters selected by the DMA are generally larger than the corresponding diameter which is needed for calculating kappa.

Fig. 3 and Fig. 5: This is a follow-up remark on the request for more physical parameterization of the hygroscopic behavior. For some activation curves the 50% activation point can be derived. E.g.: Can the observed shift in Fig 3 (filled points) be explained by the Kelvin effect or is it due to size dependent chemistry or morphology?

Fig. 4: The presented difference can either be caused by different coating thickness or by different morphology. I suspect the 2nd reason because the GFG soot is more “fluffy” (lower fractal dimension, smaller primary particle size) compared to the CAST soot. Can you confirm this hypothesis with ESM or SEM pictures?

Fig. 3 and Fig. 5: I assume that the presented activation curves are less steep than the curves for a pure model aerosol (like ammonium sulfate). Can this be explained by a variability of the composition (mixing state) of the soot particles? An analogous broadening of the growth spectra should also be seen by the HTDMA.

Figure 5: Why did you add a \sim in front of the mobility diameter in the legend?

Table 2: With the HTDMA the hygroscopic growth is classified into “not observed, shrinking”, “not observed” and a growth which can be quantified. Can this classification be quantified a bit more? When is a behavior classified as shrinking? Could it be that a particle undergoes a certain shrinking and simultaneously takes up water and is therefore classified as “not observed”?

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Table 2, 3rd experiment: 12+x%; same for minicast experiment: 78+x%.

Line 254: “instrumental error bars”: In the figures, only horizontal error bars representing the uncertainty in the RH measurement are presented. I guess that the main uncertainty in the presented data arises from errors in vertical direction (uncertainties and bias in calculating activated fractions and growth factors). Please add these as well.

Reference: Tritscher et al. (2011) Changes of hygroscopicity and morphology during aging of diesel soot *Environmental Research Letters*, 6, 034026 doi:034010.031088/031748-039326/034026/034023/034026.

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